

MLCT (METAL-TO-LIGAND CHARGE TRANSFER) SENSITIZED
INTERMOLECULAR AND INTRAMOLECULAR
PHOTOREACTIVITY OF RE (I) COMPLEXES

By

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Dedicated to Debbie, Maria and Agostino Lucia, the Carol and Lou Lentini,
the Brunos, the Cricks, and St. Augustine Catholic Student Center

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Dante Alighieri, an Italian poet, wrote his personal discovery journey in dramatic style as recounted in the epic trilogy La Divina Comedia. I can honestly say life in chemical research did at times resemble the fiction of Inferno (Hell: efforts that at times appeared damned from the get-go), Purgatorio (Limbo: waiting, waiting, and hoping the research would work) and Paradiso (Heaven: results, papers, friendly colleagues, and racing toward “Holy Grails” such as this dissertation).

I will always cherish Debra Marie Lucia, my beautiful wife, for her willingness to always lend a helping hand in all my work. I thank Kirk Schanze, my advisor, for his patient counsel and critical evaluations of all my efforts. I also thank all the denizens of Dante’s world, including Brian Hauser, Troy Bergstedt, Bruce McCosar, Ed Robinson, Yin Zhang, Rich Burton and all my friends in chemistry for all the good and bad times.

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May, 1996

Chairman: Professor Kirk S. Schanze
Major Department: Chemistry

The photophysics and photochemistry of charge-separated excited states that were generated by intramolecular photoinduced electron transfer (PET) in two chromophore-quencher systems are examined.

The first system comprises a hexacoordinate $fac\text{-}(b)\text{Re}^I(\text{CO})_3\text{Pyr}$ (where b = one of three bipyridine units: they are bpy = 2,2'-bipyridine; $dmeb$ = 5,5'-dimethoxycarboxy-2,2'-bipyridine; and tmb = 4,4',5,5'-tetramethylbipyridine; Pyr = pyridine) chromophore which is part of an ion-pair with either an inert PF_6^- counterion or the electron donor $\text{Co}(\text{CO})_4^-$ counterion. Photoexcitation of the chromophore with either of the counterions into the $d\pi(\text{Re}) \rightarrow \pi^*(b)$ metal-to-

ligand charge transfer (MLCT) manifold is followed by electron transfer from $\text{Co}(\text{CO})_4^-$ to generate two neutral radicals which can either recombine to give starting materials or go on to separate in solution. Unique to the $\text{Co}(\text{CO})_4^-$ ion-pairs is the availability of a low-energy charge-transfer absorption band which is not present in the electronic spectra of the PF_6^- ion-pair or $[\text{Na}^+, \text{Co}(\text{CO})_4^-]$. Photoexcitation into the CT manifold with 532 nm light generates the same neutral radical pair which can also recombine or separate in solution. The transient absorption spectrum of free neutral chromophore was followed for both MLCT and CT photoexcitation and it was found that the yields for the free chromophore was much higher (by a factor of 15) for MLCT vs. charge-transfer excitation. The quantum yields are quantitated and explained.

The second chromophore-quencher system that is investigated consists of a covalently linked N,N'-dimethyl-2-phenyl-3-(4-pyridine)piperazine (both *cis* and *trans* isomers) moiety attached at the N position of the pyridine to the *bpy* chromophore described above. The photochemistry and photophysics of $(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3(\text{cis-pip})^+$ and $(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3(\text{trans-pip})^+$ (*c-1* and *t-1*, respectively) were examined where *c-1** is the $\text{Re} \rightarrow \text{bpy}$ metal to ligand charge transfer excited state, *c-3* is a charge separated state where *bpy* is reduced and piperazine is oxidized, and *4* is a charge separated state where the piperazine cation radical exists as a ring opened distonic radical cation formed by fragmentation of the 2,3 C-C bond. Nanosecond laser flash photolysis of *c-1* reveals two absorbing

transients: the first is assigned to MLCT state $c-1^*$ while the second is attributed to the unique charge separated state **4**. The decay kinetics of **4** are considerably slower than typically observed for charge separated states in metal complex dyads. This unusual feature is attributed to the fact that **4** cannot decay directly to $t-1$ by charge recombination, but rather decays via a pathway involving a high energy diradical intermediate.

CHAPTER 1 INTRODUCTION

Photoinduced Electron Transfer

A molecule which absorbs light energy is a chromophore. Although chromophores were originally believed to absorb a continuum of energies, not until the early part of the twentieth century was it understood that they could absorb discrete energies [1]. Chromophores only absorb the light energy which corresponds to the energy gap between two electronic energy levels.

The transition of an electron, for example, from the singlet ground state of an organic molecule to its first singlet excited state energy level ($S_0 \rightarrow S_1$) occurs by the electronic absorption of light energy corresponding to the energy gap between S_0 and S_1 . In an organic molecule such as benzophenone, an $S_0 \rightarrow S_1$ transition may be observed in the electronic absorption spectrum obtained for benzophenone in cyclohexane [2]. An absorption band possessing a maximum wavelength of 260 nm is observed in its spectrum corresponding to a $\pi \rightarrow \pi^*$ transition (one type of $S_0 \rightarrow S_1$ transition). The maximum light energy required for the $\pi \rightarrow \pi^*$ transition in the spectrum of benzophenone is 110 kcal/mol. The

energy of the π, π^* excited state is therefore sufficient to rupture a H-H bond (104 kcal/mol) [3].

It was known in the early part of the nineteenth century that light could effect chemical change [4]. The first law of photochemistry states that *only the light which is absorbed by a molecule can produce a photochemical change* [5]. Although the energy of the π, π^* excited state for benzophenone is high in energy, no photochemical change occurs from this excited state. The energy of the π, π^* excited state is instead translated into the vibrational energy of the solvent. Excited states may engage in photoinduced electron transfer instead of dissipating their energy to the surrounding solvent molecules. Photoinduced electron transfer occurs between an excited electron donor and an electron acceptor or between an excited electron acceptor and an electron donor if the thermodynamics for electron transfer are favorable.

Photoinduced electron transfer is described by the diagram displayed in Figure 1.1. The figure shows the electronic energy levels of an electron donor (D) and an electron acceptor (A). Photoinduced electron transfer in the gas phase between two different redox pairs is illustrated by arrows. In the top figure (A), electron transfer is uphill from the ground state donor, D, to the ground state acceptor A; however, ET is downhill from the excited electron donor (D^*) and the ground state electron acceptor. Note that the lower figure is analogous to the top figure where electron transfer occurs between an excited electron acceptor (A^*)

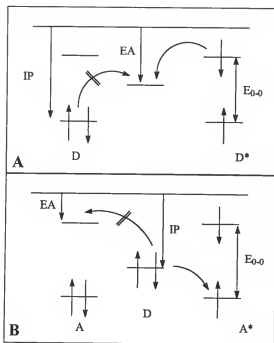


Figure 1.1. The energetic considerations for the feasibility of PET in the gas phase are shown above. In A, D^* is the excited donor, whereas in B, A^* is the excited acceptor.

and a ground state donor. Note that IP = ionization potential of the electron donor and EA = electron affinity of the electron acceptor.

The following equations are used to determine the free energy of the ET process:

$$\Delta H^{\circ}_{\text{FET}} (\text{gas phase}) = \text{IP} - \text{EA} - E_{0,0} \quad (1-1)$$

$$\Delta G^{\circ}_{\text{FET}} (\text{solution phase}) = E^{\circ}_{\text{D}} - E^{\circ}_{\text{A}} - E_{0,0} \quad (1-2)$$

$$\Delta G^{\circ}_{\text{BET}} (\text{solution phase}) = E^{\circ}_{\text{A}} - E^{\circ}_{\text{D}} \quad (1-3)$$

$\Delta H^{\circ}_{\text{FET}}$ = the enthalpy of forward electron transfer from the excited state donor to the ground state acceptor or from the ground state donor to the excited state acceptor; $\Delta G^{\circ}_{\text{BET}}$ is the free energy for back electron transfer in the redox pair to return back to the ground state donor and acceptor; E°_{D} and E°_{A} are the reduction potentials of the donor and acceptor, respectively, and $E_{0,0}$ is the energy difference between the ground and excited state of the chromophore.

In Figure 1.1A, the process of electron transfer from D to A is uphill in the ground state. The energy necessary to ionize the electron in the donor HOMO is much larger than the electron affinity of the LUMO of the acceptor; therefore, from equation (1-1) electron transfer is an endothermic process and will not occur. If, however, one of the electrons becomes promoted to an excited energy level by the light energy corresponding to the energy gap, $E_{0,0}$, electron transfer will be an exothermic process. The excess energy, $E_{0,0}$, afforded by the absorption of light

decreases the ionization potential of the donor and consequently, $\Delta G^{\circ}_{\text{FET}}$ is exothermic.

In Figure 1.1B, ground state electron transfer from the electron donor to the electron acceptor is also an uphill process. The excited state, A^* , however, has a larger electron affinity thereby allowing electron transfer to be energetically more favorable. The excess energy, E_{0-0} , afforded by light absorption to either the electron donor or acceptor therefore provides a greater opportunity for electron transfer.

Equations (1-2) and (1-3) apply to electron donor and acceptor systems in the solution phase. IP is replaced by E_D in the solution phase, whereas EA is replaced by E_A . Typically, the excited state of an electron donor or acceptor is a stronger oxidant or reductant, respectively, than its ground state by virtue of E_{0-0} [6]. The reduction potential of the excited state electron acceptor and the oxidation potential of the excited state donor in the solution phase are defined as follows:

$${}^*E^{\circ}_A = E^{\circ}_A + E_{0-0} \quad 1.4a$$

$${}^*E^{\circ}_D = E^{\circ}_D - E_{0-0} \quad 1.4b$$

In general, the excited state reduction potential of organic and inorganic molecules is 1.5 to 3.5 eV more positive than the ground state reduction potential because

excited state triplet and singlet energies are typically 1.5 to 3.5 eV above the ground state.

An Example of a System Displaying Photoinduced Electron Transfer

A brief description of photosynthesis, a classic PET system, is provided in this section. The key functions performed by the photosynthetic system are based on PET steps. Electron transfer occurs between donor and acceptor units that are roughly 20 Å apart in a protein matrix [7]. Recently, x-ray structures of the reaction centers of the synthetic bacteria, *Rps. Viridis* and *Rb. Sphaeroides* were obtained and have proven very useful for providing a sound structural basis for the interpretation of the primary events in photosynthesis [8-9].

The x-ray structure of the photosynthetic reaction center in *Rps. Viridis* is depicted in Figure 1.2. The key chromophores depicted in Figure 1.2 are the bacteriochlorophyll "special pair" (P), a bacteriochlorophyll isomer (BC) and a bacteriopheophytin (BP), a quinone (Q), and a four-heme c-type cytochrome (Cy). All of the chromophores are inside a rigid protein matrix that spans the photosynthetic membrane.

Excitation of P is followed by a very fast (3 ps) ET to the BP "primary" acceptor (the role of BC in the ET is still a subject of speculation; it may be a mediator in a superexchange mechanism) [10]. The ensuing step is also a fairly rapid (200 ps) ET from BP to Q followed by a slower (270 ns) reduction of the

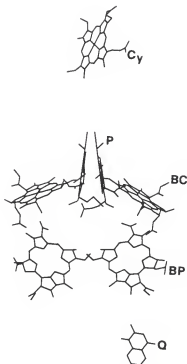


Figure 1.2. Arrangement of the chromophores in the photosynthetic reaction center of *Rps. Viridis*. The reaction center is contained within a protein matrix comprising three high molecular weight polypeptides and the active chromophores consist of the bacteriochlorophyll special pair (P), the bacteriochlorophyll monomer (BC), the bacteriopheophytin (BP), the quinone (Q), and the nearest heme group of the cytochrome (Cy).

oxidized **P** by the nearest heme group of **Cy**. At this stage, transmembrane charge-separation has been achieved with nearly unit efficiency.

Figure 1.3 shows the rate constants of the various ET steps described above. Charge recombination ($Q^- \rightarrow P^+$ electron transfer) is the slowest step in the overall charge-separation process requiring several microseconds.

The study of biological PET systems has demonstrated that molecular organization and kinetic control are critical parameters for efficient PET. Although duplication of the architecture and kinetic control of the biological photosynthetic reaction center is not presently within the scope of current scientific methodology, it is worthwhile to examine single functions of the reaction center such as the chemical conversion of light energy by photoinduced charge-separation. Remarkable success has been achieved recently in the design and synthesis of artificial multi-component supramolecular model systems for photoinduced charge-separation that mimic some of the features of the natural photosystem.

Molecular triads, for example, have been developed that consist of porphyrins (**P**) covalently linked to both carotenoid polyenes (**C**) and quinones (**Q**) [11]. Figure 1.4 illustrates a typical triad molecule, **1**, that undergoes PET to generate a charge-separated state consisting of an oxidized carotenoid moiety and a reduced quinone, $C^{\bullet+}-P-Q^-$ (**C** = carotenoid, **P** = porphyrin, and **Q** = quinone). Excitation of **P** yields the porphyrin singlet excited state, $C-^1P-Q$ (^1P = singlet

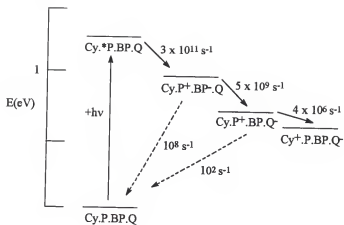
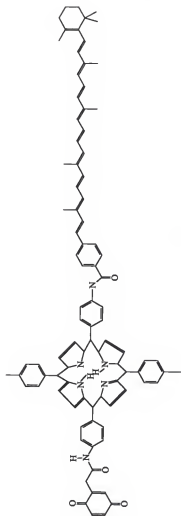


Figure 1.3. Energy level diagram with kinetic data for the photosynthetic processes that occur in *Rps. Viridis*.



1

Figure 1.4. The above molecule is an example of a typical system that mimics several fundamental photo-synthetic functions, most notably charge separation.

excited state of the porphyrin), which donates an electron to the quinone to produce the initial charge-separated state, $C-P^+-Q^-$. This state may either decay by charge recombination to return the ground state molecule, $C-P-Q$, or the carotenoid moiety may reduce the oxidized porphyrin to ultimately yield the charge-separated state, C^+-P-Q^- . Generation of C^+-P-Q^- occurs with almost unit efficiency and the charge-separated state persists for several microseconds. A lifetime of several microseconds for the charge-separated state is long enough to allow harvesting of the chemical potential energy by reaction with other species in solution or at a phase boundary [12].

Marcus Theory

Kinetic Considerations

Since electron transfer is a simple, weak interaction process where bonds are neither broken nor formed, a description of electron transfer may be presented by using a reaction coordinate based on the potential energy surfaces of the reactants and products. This reaction coordinate system shown in Figure 1.5 is derived from the semi-classical treatment of electron transfer by Marcus and later elaborated by Hush and Sutin [13-20]. Electron transfer may be defined as the crossing from the well of the reactants' potential energy surface (D,A ; D = electron donor and A = electron acceptor) to the well of the products' potential

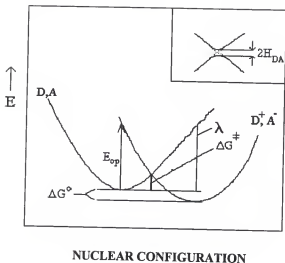


Figure 1.5. The potential energy surfaces for the reactants (D, A) and products (D^+, A^-) which describe electron transfer.

energy surface (D^+, A^- ; D^+ = oxidized donor and A^- = reduced acceptor). Marcus developed an analysis of the electron transfer process based on parabolic surfaces to relate the rate to the activation energy,

$$k_{ET} = v_N \kappa \exp(-\Delta G^*/RT) \quad (1.5)$$

where k_{ET} is the rate of electron transfer, v_N is the nuclear frequency factor, κ is the electronic transmission coefficient, ΔG^* is the free energy of activation for electron transfer at the crossing point, R is the gas constant, and T is the temperature.

Figure 1.5 aids to clarify the significance of the various terms listed above. In the figure, the nuclear configuration coordinate (the x-coordinate) defines displacements in the nuclear coordinates of the system. There are two types of nuclear coordinates: (1) inner coordinates that comprise the bond lengths and bond angles of the reactants and (2) outer coordinates that specify the arrangement of the solvent surrounding the reactants and products. The vertical axis (y-coordinate) represents the free energy displacements from the local minima while horizontal displacements represent the different equilibrium solvation shells and molecular geometries of the reactants and products.

According to quantum mechanical rules, electron transfer can only occur when the nuclei of the donor and acceptor are stationary. Thus, the Franck-Condon Principle dictates that electron transfer can only occur at the point where

the reactant and product surfaces cross; it is at this point that the states are isoenergetic. The latter geometric constraint is achieved by a distortion of the inner and outer nuclear coordinates of the reactants.

As shown in Figure 1.5, electron transfer occurs at the juncture or *crossing point* of the (D,A) reactant and (D⁺,A⁻) product potential energy curves. The transition state at the crossing point leading to electron transfer corresponds to the lowest energy pathway available in the nuclear configuration of the system.

The activation free energy, ΔG^* , is equal to the energy difference between the crossing point and the reactant minimum. The activation term, ν_N , the nuclear frequency factor, sets the maximum possible value for the rate constant. Its value is usually a weighted average of the various nuclear modes in the nuclear coordinate, but it typically is dominated by high frequency inner modes such as C-C stretching in aromatic molecules and metal-ligand stretching in coordination complexes [21-22].

As opposed to ν , the nuclear factor, κ is the electronic factor. It is known as the electronic transmission coefficient since it determines the probability of the electronic transition event between the reactant and product energy surfaces. It is related to the detailed shape of the potential energy curves at the crossing point. The reactant and product potential energy curves correspond to zero-order wavefunctions of the system. In order for electron transfer to occur, electronic interaction between the zero-order states must occur [22]. A perturbation

Hamiltonian, H_{AB} , coupling the initial and final states shown in the inset in the figure describes the extent of interaction at the crossing point. To a first approximation, electronic coupling results from the overlap of the donor and acceptor orbital wave functions.

The probability, κ , of electron transfer from the potential surface of the reactants to the potential surface of the products may be determined from the value of H_{DA} . If $H_{DA} = 0$, then there is no interaction between D and A and $\kappa = 0$ which indicates that electron transfer never occurs. If H_{DA} is small ($10^{-3} - 10^{-2}$ eV), but not equal to zero, then there is a weak interaction between D and A and κ is non-zero, but less than one. In the latter case, electron transfer occurs slowly due to poor electronic coupling. The crossing is referred to as a "weakly avoided crossing" since the probability for electron transfer is nonzero. If H_{DA} is large (> 0.01 eV), then there is a strong interaction between D and A and $\kappa = 1$. At $\kappa = 1$, electron transfer occurs every time the crossing point is reached and the electron transfer is adiabatic. The crossing is referred to as a "strongly avoided crossing" since the probability for electron transfer is unity.

It can be seen from Figure 1.5 that the activation free energy for electron transfer, $\Delta G^\ddagger$ (see eqn. 1.5) is determined by the combined effects of the degree of distortion between the reactants and products (horizontal displacement of curves) and the driving force of the reaction (vertical displacement). The above

relationship is expressed by Marcus theory in terms of a parabolic free-energy equation [23]:

$$\Delta G^* = (\lambda/4) (1 + \Delta G^0/\lambda)^2 \quad 1.6$$

ΔG^0 is the standard free energy change for ET and λ is the reorganizational energy which corresponds to the energy required to distort the reactant geometry to that of the product (minimum) while remaining on the reactant surface. The vertical energy difference between the well of the reactant curve and the product curve corresponds to the energy for optical electron transfer, E_{op} .

The reorganizational energy, λ , may be attributed to the sum of two independent contributions relating to the reorganization of inner, λ_i , and outer, λ_o , nuclear modes.

$$\lambda = \lambda_i + \lambda_o \quad 1.7$$

The reorganizational energy modes may be calculated from Marcus theory. λ_o , the outer reorganizational energy, is given by

$$\lambda_o = e^2(1/\epsilon_{op} - 1/\epsilon_s) (1/2r_D + 1/2r_A - 1/r_{DA}) \quad 1.8$$

in which the reactants are treated as spheres in a dielectric continuum. In eqn. 1.8, e is the electronic charge, ϵ_{op} and ϵ_s are the optical and static dielectric constants of

the solvent, respectively, r_D and r_A are the radii of the reactants, and r_{DA} is the distance between the centers of the reactants.

In general, λ_o increases with increasing solvent polarity and increasing r_{DA} . λ_i depends on the degree of geometrical distortion in the D/D^+ and A/A^- couples and the degree of delocalization and bonding character of the transferred electron.

The inner sphere reorganizational energy, λ_i , is defined as follows:

$$\lambda_i = \frac{1}{2} \sum_j k_j (Q_j^r - Q_j^p)^2 \quad (1-9)$$

in which Q_j^r and Q_j^p are equilibrium values (where the superscripts, r and p, refer to the reactants and products, respectively) for the jth normal mode coordinate Q , and k_j is a reduced force constant $2k_j^r k_j^p / (k_j^r + k_j^p)$ associated with it.

Marcus Inverted Region

One of the most surprising features of the Marcus theory is the behavior it predicts in the highly exoergic ΔG^0 region, known as the Marcus Inverted Region first described in 1960 [15]. The reaction rate is predicted to decrease as ΔG^0 exceeds λ . Initially, the existence of the inverted region was approached with skepticism since it directly conflicted with *linear* free energy relationships [24]. In fact, not until the middle of the 1980s did experimental evidence surface to support its existence [25-27].

The origin of the Marcus inverted region can be understood by following the crossing point as the exothermicity of the reaction becomes more negative (more negative ΔG°) shown in Figure 1.6. As shown in the figure, the normal region (left figure) encompasses reactions which are activated. In activationless electron transfer reactions (middle figure), the free energy change is equal to zero and the electron transfer reactions are very exothermic. Therefore, for moderately exothermic reactions the rate of electron transfer will increase, but for strongly exothermic reactions as shown for the right figure the rate of electron transfer is predicted to *decrease*.

Objectives of the Present Study

Two separate projects were accomplished in the present study. One is described in Chapter 2 and focuses on metal-to-ligand charge transfer (MLCT) and optical charge-transfer of organometallic ion-pairs consisting of a Re-based cation, $\text{fac}(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3\text{L}^+$ (where (bpy) = 2,2'-bipyridine, L = 4-pyridine) and $\text{Co}(\text{CO})_4^-$ as the anion. The work in Chapter 3 focuses on the photoinduced electron transfer isomerization of the ligand L = *cis*-2-phenyl-3-(4-pyridyl)-N, N'-dimethylpiperazine for the $\text{fac}(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3\text{L}^+$ complex (with PF_6^- as the counterion).

Both projects possess a common chromophore unit, $\text{fac}(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3\text{L}^+$, which absorbs near-UV light (355 nm) to access the MLCT excited state. The

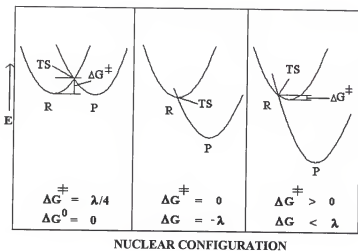


Figure 1.6. Potential energy curves for reactant (R) and product (P) states illustrating the energy ranges for Marcus theory.

MLCT excited state consists of a electron hole in the $d\pi$ orbitals of the Re atom and an odd electron on the π^* orbitals of bpy. The excited state sensitizes electron transfer from an electron donor to generate a charge-separated state. For the work in Chapter 2, the electron donor is the counterion, $\text{Co}(\text{CO})_4^+$, whereas for the work in Chapter 3, the electron donor is the piperazine ligand which is covalently attached to the Re atom.

The factors which make the MLCT state highly desirable are (1) its relatively long lifetime in polar solvents (hundreds of nanoseconds), (2) its strong luminescence, and (3) its fairly strong excited state oxidation potential (approximately 1.2 eV). The long lifetime of the MLCT state ensures that a bimolecular ET quenching process can compete with radiative and non-radiative deactivation of the state even if the rate of electron transfer quenching is relatively slow ($\approx 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). Since the $\text{Re} \rightarrow \text{bpy}$ MLCT state is strongly luminescent, the rate of forward electron quenching of the state by an electron donor can be determined by time-resolved emission spectroscopy.

Both projects attempt to obviate back electron transfer after the electron donors have quenched the MLCT state by electron transfer and thus generated a "charge-separated" state (the donor is oxidized and the acceptor is reduced). The primary objective of most photoinduced electron transfer studies is the rational design of electron-donor acceptor systems which can channel the energy of the charge-separated state into chemical change. In order to overcome back electron

transfer, subsequent processes must be faster. For the work described in Chapter 2, the energy of the charge-separated state is captured in the solvent-separated redox pair, whereas for the work in Chapter 3, the energy of the charge-separated state is captured by the isomerization of the piperazine ligand.

For both projects, the ratio of molecules that undergo “useful” chemistry versus back electron transfer is relatively high (on the order of 0.5). This is principally accounted for by the spin multiplicity of the charge-separated state. Since the state is triplet in character, it must undergo an intersystem crossing to the singlet state in order for recombination to occur. In this time, the ion-pair systems in Chapter 2 have a greater opportunity for solvent-separation, and the piperazine complexes in Chapter 3 have a greater opportunity for isomerization.

CHAPTER 2 CHARGE-TRANSFER PHOTOCHEMISTRY OF (DIIMINE)RECO ION-PAIRS

Introduction

Charge-transfer complexes have been the subject of a number of investigations in the latter half of this century [28-32]. Among the earliest and most productive research efforts in this area were those of Hildebrand and Benesi who helped to provide some useful data for the framework of charge-transfer theory. They observed that the electronic spectra of an *n*-heptane solution of benzene and iodine displayed an absorption band which was not present in the spectra of either benzene or iodine [33]. At a 1950 Symposium, Mulliken was able to provide an explanation for the occurrence of this band in terms of charge-transfer theory [34].

Before exploring the details of the theory and using it to explain charge-transfer energies, the phenomenon of a molecular complex leading to charge-transfer needs to be briefly defined. A molecular complex characterizes an electronic interaction that occurs in the ground state of two molecular species. Typically, the complex has an association that is somewhat stronger than van der

the partners in the association is relatively electron-rich (a Lewis base) and the other is relatively electron-poor (a Lewis acid).

G. N. Lewis described the formation of molecular complexes in terms of the ability to share electrons by an electron donor and an electron acceptor [35]. For example, a trialkyl amine/boron trichloride ($R_3N:BCl_3$) complex is especially stable since in the complex both the N and B atoms possess a complete octet of outer-shell electrons [35]. The electronic interaction in the ground state of a molecular complex can therefore be described by an approximate wavefunction, Ψ_{GS} , that is a combination of the wavefunctions of two resonance structures as shown in equation (2-1):

$$\Psi_{GS} \cong a\Psi_0(D, A) + b\Psi_1(D^+-A^-) \quad (2-1)$$

In the above equation, the wavefunction for the electronic interaction between an electron donor (D) and an electron acceptor (A) is described approximately as the linear combination of a no-bond wavefunction [$\Psi_0(D, A)$] and a dative wavefunction [$\Psi_1(D^+-A^-)$] which has both ionic and covalent character. The ionic aspect of this wavefunction represents the transfer of the electron from the donor to the acceptor. The transfer is considered to occur from the HOMO of the donor to the LUMO of the acceptor. For weak complexes, the contribution of the dative wavefunction is small and $b \ll a$.

Likewise, the wavefunction for the excited state, Ψ_{ES} , can be approximated as follows:

$$\Psi_{ES} \cong {}^*\mathbf{a}\Psi_1(D^+-A^-) - {}^*\mathbf{b}\Psi_0(D, A) \quad (2-2)$$

The asterisks on the coefficients denote the new contributions of the individual wavefunctions to the excited state. These coefficients must have values which allow the ground and excited state wavefunctions to be orthogonal according to quantum theory requirements. Equation (2-2) demonstrates that the contribution of Ψ_0 (the no-bond structure) to the excited state wavefunction is much less than it was for the ground state wavefunction (since ${}^*\mathbf{b} \ll {}^*\mathbf{a}$). The equation is intuitively logical since it is expected that electron transfer would occur in the excited state and the dative structure would be the dominant resonance form. From the two wavefunction expressions in (2-1) and (2-2), it is possible to derive the Mulliken relationship from which the energy of the CT can be obtained.

The function in (2-1) is normalized as follows:

$$\int \Psi_{GS} \Psi_{GS} d\tau \quad (2-3)$$

$$= \int (a\Psi_0 + b\Psi_1)^2 d\tau = 1 \quad (2-4)$$

(2-4) is then expanded to give the following:

$$a^2 \int \Psi_0^2 d\tau + b^2 \int \Psi_1^2 d\tau + 2ab \int \Psi_0 \Psi_1 d\tau = 1 \quad (2-5)$$

And since $\int \Psi^2 d\tau = 1$, (2-5) reduces to:

$$a^2 + b^2 + 2abS_{01} = 1 \quad (2-6)$$

in which S_{01} is the overlap integral, $\int \Psi_0 \Psi_1 d\tau$, that characterizes the degree of electronic overlap between the functions Ψ_0 and Ψ_1 . The energy of the ground state is given by the following quantum mechanical relationship:

$$E_{GS} = \langle \Psi_{GS} | H | \Psi_{GS} \rangle \quad (2-7)$$

This equation can be expanded by inserting equation (2-1) for the ground state wavefunction into (2-7) and obtaining the following:

$$E_{GS} = a^2 E_0 + b^2 E_1 + 2ab H_{01} \quad (2-8)$$

in which E_0 is the electronic energy of the no-bond structure (given by $\langle \Psi_0 | H | \Psi_0 \rangle$), E_1 is the electronic energy of the dative structure (likewise given by

$\langle \Psi_1 | H | \Psi_1 \rangle$), and H_{01} is the energy of overlap between Ψ_0 and Ψ_1 (given by $\langle \Psi_0 | H | \Psi_1 \rangle$).

If it is assumed that the complex interaction in the ground state is weak (a "loose" complex), then from (2-6) since $b \ll a$ and S_{01} is small (thus making H_{01} equally small), $a^2 \approx 1$. The following relationship would hold from (2-8):

$$E_{GS} \approx E_0 \quad (2-9)$$

in which the energy of the ground state is approximately equal to the energy of the no-bond structure, (D,A). It can be seen that applying the same mathematical treatment to derive eqs. (2-3) through (2-9) in order to obtain likewise the energy of the excited state, E_{ES} , would yield the following:

$$E_{ES} \approx E_1 \quad (2-10)$$

Again, the energy of the excited state is approximately equal to the energy of the dative structure, ($D^+ \cdot A^-$). To obtain the charge-transfer energy, the following equation is used

$$h\nu_{CT} = E_{ES} - E_{GS} \quad (2-11)$$

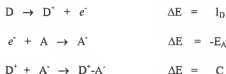
and upon combining equation (2-8) and the analogous equation for E_{ES} ($E_{ES} = a^2E_1 + b^2E_0 - 2abH_{01}$) the following relationship is obtained which is the basis for Mulliken charge-transfer theory:

$$h\nu_{CT} = E_1 - E_0 + K \quad (2-12)$$

in which K is a constant term equal to $[(H_{01} - E_0S_{01})^2 + (H_{01} - E_1S_{01})^2]/(E_1 - E_0)$. If $b \ll a$ as is the case in a weak complex, the K term in (2-12) vanishes and (2-12) reduces to

$$h\nu_{CT} \approx E_1 - E_0 \quad (2-13)$$

In order to test the CT theory by determining its ability to accurately predict charge-transfer energies, it is necessary to relate the energy difference between the dative structure (principally found in the excited state) and the no-bond structure (principally found in the ground state) to experimentally determine ionization potentials (I_D) of the donor, D, electron affinities (E_A) of the acceptor, A, and coulombic energy, C , released in order to bring the ions together in an equilibrium configuration. Thus, consider the stepwise CT process:



Therefore, the overall electron transfer process for



has energy

$$E_1 - E_0 \approx I_D - E_A + C \quad (2-14)$$

and from (2-13) and (2-14) the energy of the CT is approximated as follows [36]:

$$h\nu_{CT} \approx I_D - E_A + C \quad (2-15)$$

Note that (2-15) neglects the K term from (2-12). The above Mulliken relationship contains a wealth of information about the influence of the donor and acceptor strength on the charge-transfer energy. For instance, among a group of charge-transfer complexes which have a common electron acceptor, the charge-transfer energy will decrease as the ionization potential of the donor decreases (assuming

E_A and C remain constant). Likewise, among a group of charge-transfer complexes that have a common electron donor, the charge-transfer energy will decrease as the electron affinity increases (again, assuming I_D and C remain constant). Several examples will be given in the next section dramatically highlighting the Mulliken relationship for both organic electron-donor acceptor complexes and inorganic ion-pair charge-transfer complexes

Application of Mulliken Theory to Charge-Transfer Complexes

Mulliken theory can be applied to the charge-transfer behavior of various electron-donor acceptor complexes. A schematic representation of the qualitative manner in which the members of the complex interact is provided in Figure 2.1. Complex A illustrates a tetracyanoethylene (TCNE) electron acceptor and a benzene electron donor in a π - π stacking arrangement and Complex B illustrates the ion-pair CT complex between a quinolinium ion acceptor and a tetracarbonylcobaltate ion donor. The strength of the interaction in Complex A according to Mulliken theory depends on both the ionization potential of the donor, benzene, the electron affinity of TCNE, and the coulombic energy of interaction. If a series of electron-donor acceptor complexes having the same acceptor, TCNE, are compared, it can be shown that the energy of the charge-transfer can be correlated to Mulliken theory.

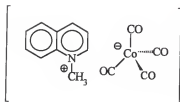
**A****B**

Figure 2.1. Scheme for the EDA complex **A** illustrates a π - π interaction which is available between benzene (the electron donor) and tetracyanoethylene (the electron acceptor). **B** is the ion-pair CT complex for an N-methylquinolinium ion and a tetracarbonylcobaltate ion.

Shown in Table 2.1 are the energies of the charge-transfer absorption band for a series of alkylbenzene electron donors that have a common electron acceptor, tetracyanoethylene. Since the electron affinity of the acceptor remains constant throughout the series of electron-donor acceptor complexes (as well as the coulombic energy due to the structural similarity of the donors), the charge-transfer energy ($h\nu_{CT}$) may be obtained as follows:

$$h\nu_{CT} \approx E_{1/2}(D/D^+) + K \quad (2-16)$$

$E_{1/2}(D/D^+)$ is the oxidation potential for an alkylbenzene and may be substituted in the solution phase for I_D (the gas phase ionization potential of the electron donor). K is a constant for each electron-donor acceptor system since the same acceptor is being used. A plot of $h\nu_{CT}$ versus $E_{1/2}$ is shown in graph A of Figure 2.2 and clearly shows a very good linear relationship between $h\nu_{CT}$ and $E_{1/2}$. The charge-transfer energy increases as the alkylbenzene electron donor becomes harder to oxidize ($E_{1/2}$ goes to larger positive values).

The Mulliken theory not only applies to a series of donors with a common acceptor, but it can also be shown to apply to a series of acceptors with a common donor. The charge-transfer energy from (2-15) may also be related to the electron affinity of the electron acceptor in the following equation:

Table 2.1. CT energies of EDA complexes in CH_2Cl_2 calculated at the maximum wavelength of absorption for the charge-transfer band. Tetracyanoethylene is the electron acceptor in each case.

Electron Donor	$E_{1/2}^a$ V, SCE	λ_{max}^b nm	$h\nu_{\text{CT}}$ eV
Benzene	2.30	391	3.17
Methylbenzene	1.98	406	3.06
1,4-dimethylbenzene	1.77	460	2.70
1,3,5-trimethylbenzene	1.80	467	2.66
1,2,4,5-tetramethylbenzene	1.62	480	2.58
Hexamethylbenzene	1.52	541	2.29

Note: Electrochemical oxidation potentials were obtained from Encyclopedia of Electrochemistry of the Elements (Organic Section): Vol. XI, p. 48; Eds. Allan J. Bard and Henning Lund; Marcel Dekker, Inc.: 1978, New York.

^a Potentials were obtained by polarography in acetonitrile using a rotating Pt electrode and an SCE reference electrode.

^b CT energies were obtained from CT Photochemistry of Coordination Compounds; Ottó Horváth; Kenneth L. Stevenson; VCH: New York, 1993.

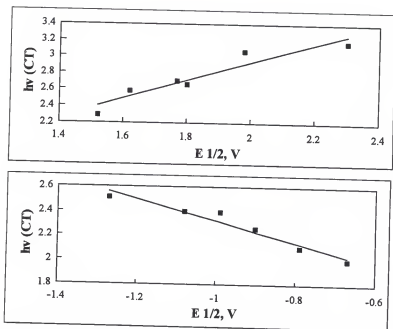


Figure 2.2. Mulliken relationship for a series of alkylbenzene donors (top plot, see Table 2.1 for data) and a series of pyridinium electron acceptors with a common $\text{Co}(\text{CO})_4^-$ electron donor (bottom plot, see Table 2.2 for data).

$$h\nu_{CT} \approx -E_{1/2}(A/A^{\cdot-}) + K \quad (2-17)$$

In the above equation, the reduction potential of the electron acceptor has been substituted for the electron affinity, E_A . Table 2.2 lists the charge-transfer energy for a series of pyridinium ion electron acceptors with a tetracarbonylcobaltate ion electron donor studied extensively by Kochi and Bockman [37]. The structures for the pyridinium ions whose abbreviations are used in Table 2.2 are shown in Figure 2.3. It is readily apparent that the charge-transfer energy decreases as the pyridinium ions become easier to reduce (the values become less negative) according to the Mulliken relationship shown in eq. 2-17. The plot of $h\nu_{CT}$ versus $E_{1/2}(A/A^{\cdot-})$ is shown in Figure 2.3 and like the organic EDA systems also obeys the Mulliken relationship. The slopes of the two plots are very close to unity as implied by Mulliken theory (2-15); the slope of the plot with pyridinium cations is -0.89 V^{-1} , whereas for the plot with Re cations the slope is -1.12 V^{-1} .

Table 2.2 has a column which lists the K_{ip} (equilibrium constant values) for the various ion-pair charge-transfer systems. For all charge-transfer systems, there exists an equilibrium between the contact pair (in this case, the contact ion-pair) and the solvent-separated pair which ultimately proceeds to free species in solution. The next section explores the equilibria charge-transfer systems undergo, with particular emphasis on ion-pair charge-transfer complexes which have a tetracarbonylcobaltate ion $[\text{Co}(\text{CO})_4]^-$ electron donor. $\text{Co}(\text{CO})_4^-$ is an excellent

Table 2.2. CT energies of the charge-transfer ion-pairs in CH_2Cl_2 . Tetracarbonylcobaltate ion is the electron donor in each case.

Electron Acceptor ^a	$E_{1/2}$ (eV, SCE)	λ_{max} (nm)	$h\nu_{\text{CT}}$ (eV)	K_{ip}^b (M)	ϵ^c ($\text{M}^{-1}\text{cm}^{-1}$)
PP^+	-1.27	494 (442) ^d	2.51	2.3×10^{-5}	380
$i\text{-Q}^+$	-1.08	516 (510)	2.40	-	-
Cp_2Co^+	-0.99	520 (508)	2.39	1.5×10^{-4}	230
Q^+	-0.90	550 (520)	2.26	1.5×10^{-5}	590
CMP^+	-0.79	590 (590)	2.10	-	-
NCP^+	-0.67	620 (560)	2.00	-	-

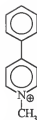
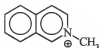
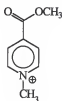
Note: All data was obtained from Advances in Organometallic Chemistry: Vol. 33; Organometallic Ions and Ion Pairs; Jay K. Kochi and Michael Bockman, p. 51; Eds. F.G.A. Stone and Robert West; Academic Press, Inc.: 1991, New York.

a See Figure 2.3 for structures of the acceptors.

b Equilibrium constants for ion-pairs; see Scheme 2-1 for illustration.

c The extinction coefficient at the CT max.

d Maximum of CT absorption band obtained from the diffuse reflectance spectrum is displayed in parentheses for all the ion-pairs. The maxima are obtained from 10% dispersions in silica.

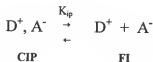
**PP⁺****Cp₂Co⁺*****i*-Q⁺****Q⁺****CMP⁺****NCP⁺****Figure 2.3.** Structures of the cations used in Table 2.2.

electron donor ($E_{1/2} = +0.33$ eV vs. SSCE) [38] that undergoes electron transfer with the cations of the ion-pairs in this study (See Table 2.3 for the free energies of ET with selected cations).

Equilibrium of Charge-Transfer Systems

Since charge-transfer systems by definition consist of an electron donor and an electron acceptor, unless they are covalently bound, they undergo by necessity an intermolecular process in solution to attain a geometry conducive to charge-transfer. Typically, the members of the charge-transfer system are subject to a dynamic equilibrium which is depicted in the following scheme for ion-pairs:

Scheme 2-1



Scheme 2-1 illustrates the equilibrium of the charge-transfer ion-pair in solution between the CIP (contact ion-pair) and the FI (free ions). An elegant analysis of the ion-pair equilibria shown in (2-1) above was provided by Winstein who formulated the concept of a contact ion pair, **CIP**, that may be penetrated by solvent molecules to attain the solvent separated ion-pair, **SSIP** (not shown since it

cannot be detected in this study), from which the members of the pair can diffuse into solution as free ions, **FI** [39-41].

The equilibrium between **CIP** and **FI** in various solvents can be evaluated spectrophotometrically by measuring the change in the CT absorbance $A_{(CT)}$ at various concentrations C of the charge transfer salt and applying the following relationship [42-43]:

$$K_{ip} = A_{(CT)}/\epsilon_{(CT)} + (C^2) \epsilon_{(CT)}/A_{(CT)} - 2C \quad (2-3)$$

From Scheme 2-1, K_{ip} is the equilibrium constant for the dissociation of the **CIP** to the **FI** (Units: M), $A_{(CT)}$ is the absorption of the salt at the CT band maximum, $\epsilon_{(CT)}$ is the extinction coefficient at that wavelength (units: $M^{-1}cm^{-1}$), and C is the concentration of the salt (units: M). Application of this formula to several of the ion-pairs shown in Table 2.2 gives K_{ip} 's which strongly favor **CIP** (1×10^{-5} M for $[Q^+, Co(CO)_4]$ to 1.5×10^{-4} M for $[Cp_2Co^+, Co(CO)_4]$) and also extinction coefficients that are relatively low ($380 M^{-1}cm^{-1}$ for $[PP^+, Co(CO)_4]$ to $590 M^{-1}cm^{-1}$ for $[Q^+, Co(CO)_4]$). In general, the equilibrium tends to strongly favor the charge-transfer ion-pair in low polarity solvents such as CH_2Cl_2 . Other spectroscopic tools which may provide a means to probe the equilibrium and the extent of interaction involved in ion-pairs listed in Table 2.2 include IR and x-ray crystallography.

Kochi has suggested that infrared (IR) spectroscopy is an important diagnostic tool that may be used to probe the equilibrium for an ion pair such as $[Q^+, Co(CO)_4^-]$ by examining the carbonyl stretching frequencies of the tetracarbonylcobaltate ion [37, 44]. An isolated tetracarbonylcobaltate anion displays a highly symmetrical tetrahedral structure which on the basis of group theory is expected to exhibit one stretching frequency in the IR [44]. Consistent with this rationalization, an undistorted tetracarbonylcobaltate ion in the solid phase has a carbonyl stretching frequency at 1883 cm^{-1} [45]. In an IR spectrum of $[Q^+, Co(CO)_4^-]$ in a 10 % by mass KBr pellet, three carbonyl bands were observed at 2007 (2004), 1928 (1910), and $1895\text{ (1887)}\text{ cm}^{-1}$ (the values in parantheses were obtained in THF solution) [46]. These bands are obtained as a result of the distortion of the anion from a T_d (tetrahedral) symmetry to a C_{3v} (a three-fold axis and horizontal plane of symmetry) symmetry as determined from x-ray C-Co-C angles. This distortion arises due to an electronic interaction between the ions which is only possible in the CIP.

An x-ray structure of $[Q^+, Co(CO)_4^-]$ has a configuration in which the tetracarbonylcobaltate ion lies above the aromatic plane of the quinolinium ion. An ORTEP diagram of the x-ray structure of the ion-pair is provided in Figure 2.4 [46]. The geometry of the interaction between the cation and the anion causes the anion to assume a C_{3v} symmetry. One of the more important experimental results relating to the geometry of $[Q^+, Co(CO)_4^-]$ in solution is the correspondence

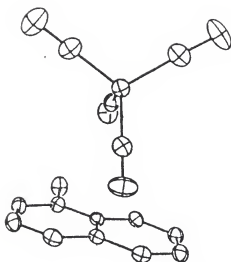


Figure 2.4. ORTEP diagram of $[\text{Q}^+, \text{Co}(\text{CO})_4]^+$ (See Figure 2.2) illustrating the relevant charge transfer interaction between the tetracarbonylcobaltate ion and the aromatic π system of the quinolinium cation.

between the anionic carbonyl IR bands obtained in the solid and non-polar solvents (such as THF). For $[Q^+, Co(CO)_4^-]$, the same carbonyl IR bands observed in the solid phase work (*vide supra*) are observed in solutions of the ion-pair in THF. This result would lend support to the conclusion that the interaction present in the solid may likewise be in the CIP. It is logical to assert that solvent interpenetration of the CIP weakens the electronic interaction between the anion and the cation (in the FI) and decreases the perturbation of the tetracarbonylcobaltate ion. An IR spectrum taken of $[Q^+, Co(CO)_4^-]$ which is principally in the SSIP state (or FI) should therefore reveal only one carbonyl stretch for the anion. In a highly polar solvent such as acetonitrile, the equilibrium for $[Q^+, Co(CO)_4^-]$ is expected to shift more toward the FI as evidenced by a calculated K_{sp} value of 8.1×10^{-2} M (as opposed to 1.2×10^{-4} M in THF). The IR in acetonitrile for the latter ion-pair reveals that only one carbonyl IR band is observed at 1892 cm^{-1} . Indeed, for all of the ion-pairs in Table 2.2, IR spectra conducted in acetonitrile show only one carbonyl IR band corresponding to the tetracarbonylcobaltate ion in the T_d symmetry.

Description of the Charge-Transfer Systems Used in This Study

The CT systems which have been the focus of this work consist of a $[(b)Re^I(CO)_3pyridine^+]$ cation (where (b) is a diimine ligand) and a tetracarbonylcobaltate ion, $Co(CO)_4^-$. Figure 2.5 shows the structures of both the

cation and the anion along with the abbreviations of the three different ion-pairs used throughout the text. Like all the charge-transfer systems shown in Tables 2.1 and 2.2, the ion-pairs shown in Figure 2.5 display a low-energy charge-transfer absorption band which is absent in the UV-vis spectra of the starting materials of the ion-pair.

In order to understand the rationale for the choice of the cation in these systems, attention must be given to the photophysical properties of the metal-to-ligand CT (MLCT) excited state of the cation.

The MLCT excited state is populated by irradiating the cations shown in Figure 2.5 with near-UV light (355 nm). Upon absorption of the light energy, an electron is transferred from the $d\pi$ orbitals of the Re to the low-lying π^* orbitals of the covalently attached diimine (leaving a "hole" in the $d\pi$ orbitals of the Re). This excited state is normally long-lived (on the order of several hundred nanoseconds) and decays either non-radiatively or by emission of a photon concomitant to return of the electron in the π^* orbital of the diimine to the $d\pi$ orbital at Re. Electron transfer quenching of the MLCT excited state requires that the transfer of an electron from an electron donor (the quencher) occurs within the lifetime of the excited state. In the MLCT excited state, the electron hole that resides in the $d\pi$ orbitals of the metal can accept an electron from an appropriate electron donor. The excited state reduction potential of the MLCT state is on the

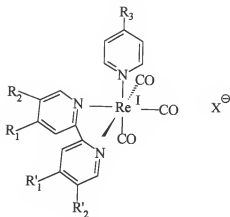


Figure 2.5. Structure of the ion-pairs used in the studies presented in this work. The acronyms used throughout the text for each of the ion-pairs are listed below.

R_1	R'_1	R_2	R'_2	R_3	X	Acronym
-H	-H	-Ester ^a	-Ester	-H	$\text{Co}(\text{CO})_4^-$	1
-H	-H	-Ester	-Ester	-H	PF_6^-	1a
-H	-H	-H	-H	-H	$\text{Co}(\text{CO})_4^-$	2
-H	-H	-H	-H	-H	PF_6^-	2a
-CH ₃	-CH ₃	-CH ₃	-CH ₃	-CH ₃	$\text{Co}(\text{CO})_4^-$	3
-CH ₃	-CH ₃	-CH ₃	-CH ₃	-CH ₃	PF_6^-	3a
-H	-H	-H	-H	-PyrMe ^b	$(\text{PF}_6^-)_2$	4

^a -Ester = carbomethoxy

^b -PyrMe = 4-(N-methylpyridinium)

order of +1.2 V vs. SCE, which is strong enough to allow for rapid electron transfer from electron donors having oxidation potentials $\leq +1.0$ eV vs. SCE. Table 2.3 lists the electrochemical and spectroscopic data for the MLCT excited state of various Re cations. The table also contains the free energies for the electron transfer quenching of the MLCT excited states of the Re cations by $\text{Co}(\text{CO})_4^-$. The MLCT state of the cations in Figure 2.5 have been extensively exploited in photochemistry for sensitizing electron transfer reactions [47-52].

Ion-pair Charge Transfer Scheme

A kinetic scheme describing the different processes the ion-pairs in Figure 2.5 can undergo is now presented. Figure 2.6 shows the various pathways available to the ion pair to generate a neutral radical pair (similar to the CIP) which can then normally proceed to the SSIP. 1 and 2 represent the FI and the CIP, respectively, that exist in equilibrium. The rate constant k_{ip} is the rate constant for formation of the CIP, 2, whereas k_{-ip} is the reverse rate constant to the FI, 1. In 1, $(b)\text{Re}(\text{I})^+$ represents the cation which as discussed earlier may absorb 355 nm light to populate the MLCT excited state represented as $(b^*)\text{Re}(\text{II})^+$. The ion pair with $(b^*)\text{Re}(\text{II})^+$ may partition between an associated ion pair, 4, and free ions, 3. 3 and 4 have available pathways to decay for $(b^*)\text{Re}(\text{II})^+$. In 3, decay of the excited state occurs by fluorescence which has a rate equal to

Table 2.3. The spectrochemical and electrochemical data of the cations in the present study.

Ion-Pair	$E_{1/2}(A/A^+)^a$ eV	E_{0-0}^b eV	τ^c ns	ΔG_{FET}^d eV	ΔG_{BET}^e eV	Φ_{em}^f
1a	-0.67	2.15	75	-1.15	-1.00	-
2a	-1.16	2.38	224	-0.89	-1.49	0.055
3a	-1.39	2.57	1450	-0.85	-1.72	-

a The values are taken from analogous compounds, the (b)ReB complexes shown in *J. Am. Chem. Soc.* **1991**, *113*, 7470. These values are not expected to differ much from the ion-pairs shown. The values are the one-electron reduction potentials of the diimine ligand, A, of the ion-pair cation. All work was done in CH₃CN with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

b E_{0-0} is the estimated 0-0 emission energy. See reference above for details.

c Emission lifetimes in degassed CH₃CN.

d The free energy for photoinduced forward electron transfer, ΔG_{FET} , is calculated for the cations of the ion-pair (electron acceptors) and a tetracarbonyl cobaltate ion (abbreviated as D, the electron donor) which has a $E_{1/2} = +0.33$ eV [49]. ΔG_{FET} is equal to $E_{1/2}(D^+/D) - E_{1/2}(A^+/A) - E_{0-0}$.

f The emission quantum yield measured in CH₃CN.

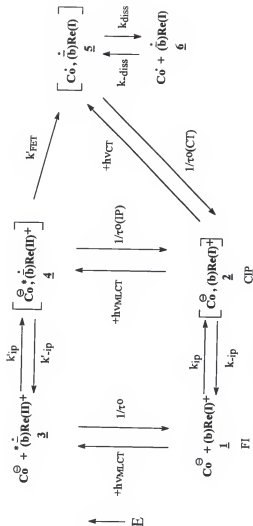


Figure 2.6. Above is depicted a typical scheme for the events which can occur in the CT ion pairs upon MLCT or CT photoexcitation. The cation of the ion-pair is depicted as $(\text{b})\text{Re}(\text{I})^{+}$ in which (b) = diimine, the anion is depicted as $\text{Co}^{\ominus}$. FI and CIP are acronyms for Free ions and Contact ion-pair, respectively.

$1/\tau^0$. This would be equivalent to the decay of free $(b^*)\text{Re(II)}^+$; however, the excited state of **4** not only has a fluorescence decay pathway available to it, but $(b^*)\text{Re(II)}^+$ may be quenched by forward electron transfer (FET) from Co^- in the CIP, **4**. This step which has a rate constant represented by k_{fet} generates a neutral radical pair, **5**. This radical pair may then dissociate into solution to yield FI, **6**, or it can undergo back electron transfer (BET) to regenerate the original ion pair.

2 has a low-energy charge-transfer absorption band available to it in addition to the local excited state of $(b^*)\text{Re(II)}^+$. The CT state is directly accessed by irradiating the ion-pair charge-transfer absorption band which is assumed to not overlap the MLCT absorption band of $(b^*)\text{Re(II)}^+$. Analogous deactivation pathways are available to **5** as observed in **4**. **5** may decay back to **2** (thermally or radiatively) or it may go on to FI, **6**.

One of the most important features of this scheme lies in the two distinct excitation avenues available to generate the same free radical species (**6**). This ion-pair system illustrates two different excitation states which can sensitize ET to bring about the same radical products (**6**). $(b^*)\text{Re(II)}^+$ is an excitation state available only to $(b)\text{Re(I)}^+$ in the pair, but the CT state is available as a result of the interaction between $(b)\text{Re(I)}^+$ and Co^- .

Objective of the Present Study

The ion-pairs shown in Figure 2.5 were developed to study the differences in free ion yields between exciting into the MLCT manifold of the cation versus exciting into the charge-transfer band of the ion-pair (refer to Figure 2.6).

In the figure, 2 may be excited by 350 nm light to directly populate the MLCT state of the cation. This excited state possesses triplet spin character. When Co^- is intimately associated with $(b')\text{Re(II)}^+$ as in 4, quenching of the MLCT excited state may occur since the oxidation potential of the anion is very low (0.3 eV) [49]. The neutral radical pair that is produced, 5, must therefore have triplet spin character after FET. On the other hand, excitation of 2 with 532 nm light will directly afford the neutral radical pair, 5. This state, however, although represented as the same neutral radical pair, is generated as the singlet state. Therefore, the subsequent diffusional sequence available to 5 will depend on which excitation route was followed to generate it. A triplet state will persist for a much longer time than a singlet state because spin recombination is a forbidden process. 5 generated from 4 must therefore undergo an intersystem crossing to a singlet prior to recombination. The increased lifetime of the triplet state provides a greater time window for dissociation (k_{dis}) to 6 than is possible from the singlet state of 5. Thus, increased overall yields of FI should be observed for MLCT versus charge-transfer photoexcitation of the ion-pairs in Figure 2.6.

Results

UV-Visible Absorption Spectra

UV-Vis spectra were obtained for all complexes in THF which was distilled over Na/K and benzophenone. All spectra were referenced to THF blank solutions that had been "zero-referenced" at 800 nm. All solutions of the CT ion-pairs were prepared in a nitrogen atmosphere drybox with less than 10 ppm of oxygen. Typically, the solutions of charge-transfer ion-pairs were transferred to quartz cuvettes, sealed with rubber septa and absorption spectra were obtained of the solutions in the dark to prevent photolysis of the charge-transfer ion-pair.

The structures and abbreviations for all of the complexes which were analyzed in this study are shown in Figure 2.5.

As displayed in Figure 2.7, **1**, **2**, and **3** as well as **1a**, **2a**, and **3a** possess strong absorbances ($\epsilon \cong 2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) in the ultraviolet (UV) region (between 300 and 340 nm) which are a result of intraligand π^* , π^* transitions on the diimine ligand. These strong UV bands tail off into absorbance bands that are broader and much lower in intensity in the near-UV (350–400 nm).

In each ion-pair, the near-UV band has an extinction coefficient at 350 nm that is approximately $4,000 \text{ M}^{-1}\text{cm}^{-1}$. The broad, moderately intense bands found at 350 nm for **1-3** and **1a-3a** have been previously attributed to a metal-to-ligand charge transfer (MLCT). The MLCT absorption arises as a result of the transfer of

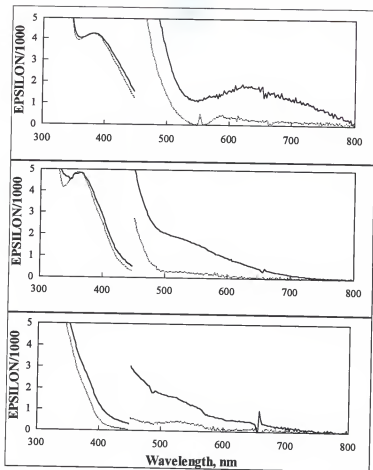


Figure 2.7. Absorption spectra for the Co(CO)_4^- ion-pairs 1 (top), 2 (middle), and 3 (bottom) are displayed as solid lines along with corresponding PF_6^- salts 1a, 2a, and 3a which appear as the dotted lines. In each case, the region of the spectra from 450 to 800 has been expanded by ten. The absorbance is plotted as molar absorptivity (EPSILON) in units of $\text{M}^{-1}\text{cm}^{-1}$.

an electron from the $d\pi$ orbitals of Re to the π^* orbitals of the diimine ligand [53]. The MLCT band is always sharply reduced in intensity at approximately 450 nm for all the complexes. In **2** and **2a** the strong, relatively narrow band at 360 nm is the MLCT band. The band essentially retains the same shape and energy in the charge-transfer complex, **2**, as in **2a**.

3, however, does not display a distinct MLCT band. In fact, the MLCT band is more blue-shifted than the analogous *hpy* complex, **2**, and is subsumed by the tail of the intraligand absorption band.

The MLCT band for **1** bears a strong resemblance in terms of band maximum (360 nm), shape, and energy to that of **2**.

As observed in Figure 2.7, the similarity of the absorption spectra between **1-3** and **1a-3a** does not extend into the visible portion of the spectrum. Low-energy, weak ($\epsilon < 500 \text{ M}^{-1}\text{cm}^{-1}$), and broad optical bands are observed in the spectra of **1-3**, but not in **1a-3a**. Due to their energy and shape in the absorption spectra of **1-3** their absence in **1a-3a**, these bands are ascribed to a charge-transfer interaction between the Re cation and the Co anion.

One outstanding piece of evidence which supports charge-transfer in **1-3** is their contrast in color versus **1a-3a**. **1-3** are red to reddish-orange in color versus the yellow to orange-yellow of the starting materials for the Re cation of the charge-transfer ion-pairs (the precursor of Co anion, $[\text{Na}^+, \text{Co}(\text{CO})_6^-]$ is white). The color of these charge-transfer ion-pairs is associated with the charge-transfer

band that is observed in the visible. The spectrum of **2** always shows an absorption band from 480nm to 725nm which is not present in the absorption spectrum for **2a**. This absorption band is broad and fairly weak and is subsumed by the MLCT band. **3** also displays a charge-transfer band that extends from about 450 nm to 700 nm which is also not present in **3a**. This charge-transfer band in **3** is even more blue-shifted than observed in **2** and is also somewhat weaker by about a factor of two. It is difficult to determine where the maximum is for **2** and **3** since the maxima of the charge-transfer bands are within the MLCT band.

Unlike **2** and **3**, **1** has a charge-transfer band that is very well defined as shown in Figure 2.7. The charge-transfer band in **1** is red-shifted relative to **2** by almost 150 nm and has a clearly pronounced maximum at 630 nm. As evidenced by the spectrum, **1a** has no absorbance in this region indicating that this absorbance of **1** is due to a charge-transfer interaction of lower energy than **2** or **3**.

The energy and intensity of the charge-transfer band is strongly affected by the polarity of the solvent. In Figure 2.8, the absorption spectra of **2** are shown in CH₃CN, THF, and benzene. In highly polar solvents such as acetonitrile, the charge-transfer band is not observed because of an unfavorable K_{ip} ; however, in less polar solvents, the K_{ip} is more favorable and a charge-transfer band is always observed for **2** in THF and benzene. The maximum of the charge-transfer band is observed to increasingly redshift as the polarity of the solvent decreases (as evidenced by the spectra of **2** in THF and benzene).

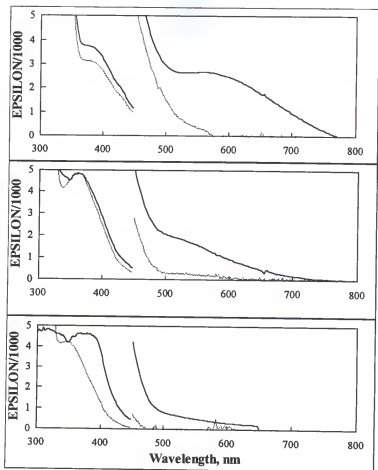


Figure 2.8. Absorption spectra for ion-pair 2 shown in benzene (top), THF (middle) and CH_3CN (bottom) are displayed as whole lines with corresponding PF_6^- salts which appear as dotted lines. In each case, the region of the spectra from 460 to 800 has been expanded by ten. The absorbance is plotted as molar absorptivity (EPSILON) in units of $\text{M}^{-1}\text{cm}^{-1}$.

According to Scheme 2-1 in the Introduction, an equilibrium exists between the ion-pair and the solvent-separated ion-pair. It is assumed that the electronic interaction between the solvent-separated ions is as small as that between the free ions; therefore, the equilibrium is essentially between an electronically coupled and a non-coupled state. In order to obtain the K_{ip} (equilibrium constant) for this equilibrium, a graphical method was chosen that was first developed by Benesi and Hildebrand [42] and later modified by Drago and Rose [43].

First of all, the graphical method relies on obtaining absorption spectra of the ion-pair at a series of increasing concentrations. Shown in Table 2.4 are the absorptions obtained at 532 nm for THF solutions of **2** of increasing concentration.

The A_{532} values and concentrations shown in Table 2.4 for solutions 1 through 9 are used as the constants in constructing a series of equations:

$$K_{ip} = A_{532}/\epsilon_{532} + C^2\epsilon_{532}/A_{532} - 2C \quad (2-18)$$

in which A_{532} = absorption at 532 nm, ϵ_{532} = extinction coefficient at 532 nm, and C = concentration. A plot of K_{ip} versus ϵ_{532} is obtained for each solution (1-9) by inserting a series of ϵ_{532} values ranging from 50 to 300 $M^{-1}cm^{-1}$ into (2-18) along with the respective constants A_{532} and C obtained for each solution. Nine different plots were generated (K_{ip} vs. ϵ_{532}) and plotted on the same graph. The results are

Table 2.4. Absorptions at 532 nm for solutions with increasing concentration of **2** in THF. Data used to develop a Drago-Rose plot.

Solution	[2]/M $\times 10^{-3}$	Absorption ^a (532 nm)
1	0.16	0.02
2	0.40	0.06
3	0.58	0.10
4	1.00	0.18
5	1.20	0.21
6	2.30	0.40
7	2.50	0.46
8	2.90	0.52
9	6.24	1.20

^a 1 cm pathlength.

shown in the upper graph of Figure 2.9. An expansion of the region where the individual plots appear to converge is shown in the lower graph of the figure.

Inherent in the determination of K_{ip} is judgement error since K_{ip} is located by visual inspection. The lower graph shown in Figure 2.9 which shows the expansion of the absorption curves obviously does not have a single intersection point among the plots. Instead they intersect at a variety of points in an area which can be circumscribed by a rectangle. A rectangle was drawn that incorporated the four most prominent regions of intersection among the curves and the center of this rectangle was assumed to be the point which contained both K_{ip} and ϵ_{532} . The center was obtained from the intersection of lines drawn connecting opposite vertices of the rectangle.

An estimate of the error for K_{ip} was determined as follows: The upper and lower K_{ip} values of the rectangle were assumed to be the limits of the error for K_{ip} . For all of the charge-transfer ion-pairs, this error was no more than a factor of five of the measured K_{ip} . However, as observed in Figure 2.9, a smaller error is associated with the determination of ϵ_{532} for the ion-pairs. The curves did not deviate more than 10% from the measured values. Values of K_{ip} and ϵ_{532} with their error limits are displayed in Table 2.5 for all of the ion-pairs.

Although the graphical determination of K_{ip} for each of the ion-pairs was repeated several times, an error of a factor of ten from the true value is possible since the measurement relies on approximation. An error of a factor of ten for the

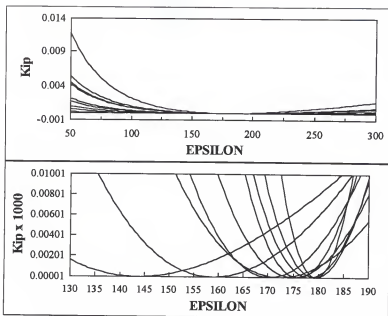


Figure 2.9. The top graph is a Drago-Rose plot for 2 in THF used to determine the extinction coefficient, ϵ , in terms of $M^{-1}cm^{-1}$, and K_{ip} , the equilibrium constant. The bottom graph is an expansion of the region between 130 and 190 $M^{-1}cm^{-1}$ of the top plot.

Table 2.5. Absorption titration data obtained in THF for 1, 2, and 3.

Complex	$K_{ip}/M \times 10^{-6}$	ϵ_{532} ($M^{-1}cm^{-1}$)	λ_{max}^* (nm)	ϵ_{max} ($M^{-1}cm^{-1}$)
1	6.0 ± 3	179 ± 10	630 ± 10	320
2	3.0 ± 6	180 ± 10	525 ± 25	230
3	2.0 ± 4	100 ± 10	425 ± 10	120

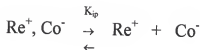
Note: The wavelength used for all the complexes to calculate the K 's and ϵ 's was 532 nm. ϵ_{max} values are extrapolated from 532 nm to band maximum.

a λ_{max} was approximated since the maxima of the CT bands are obscured by the MLCT bands.

determination of K_{ip} would substantially affect the calculation of the degree of ion-pairing for a particular ion-pair concentration.

Scheme 2-1 may be written as Scheme 2-2 to be specific to the present system; in Scheme 2-2, Re^+ represents the $(diimine)Re(CO)_3(pyridine)^+$ cation, and Co^- represents the $Co(CO)_4^-$ anion.

Scheme 2-2



For the above equilibrium shown in Scheme 2-2, the fraction of ion-pairing, α , is defined as follows:

$$\alpha = 1 - [Re^+]/[Re^+, Co^-] \quad (2-19)$$

where α is the fraction of Re^+ in the ion-pair state. The equilibrium expression for the equilibrium in Scheme 2-2 is defined as follows:

$$K_{ip} = [Re^+][Co^-]/[Re^+, Co^-] \quad (2-20)$$

and since $[\text{Re}^+] = [\text{Co}^-]$ equation (2-20) is equivalent to:

$$K_{ip} = [\text{Re}^+]^2/[\text{Re}^+, \text{Co}^-] \quad (2-21)$$

and if $[\text{Re}^+]$ is expressed as a variable, x , then (2-21) may be expressed as follows:

$$K_{ip} = x^2/([\text{Re}^+, \text{Co}^-] - x) \quad (2-22)$$

Equation (2-22) may be solved by the quadratic equation. At any concentration of $(\text{Re}^+, \text{Co}^-)$, the fraction of ion-pairing as given by (2-19) may be calculated since K_{ip} is known (see Table 2.5), the concentration of $(\text{Re}^+, \text{Co}^-)$ is known (the starting concentration in solution), and since $x = [\text{Re}^+]$, $[\text{Re}^+]$ is obtained by solving for x in (2-22) by the quadratic equation.

Plots of the fraction of the ions in the ion-pair state, α , versus the log of the concentration of $(\text{Re}^+, \text{Co}^-)$ were obtained at three different values of K_{ip} and are shown in Figure 2.10. Note that the middle line was obtained by using the value of K_{ip} determined from the graphical method described above (3×10^{-6}) and the top and bottom plots were obtained by using values of K_{ip} that were a factor of ten smaller and larger, respectively.

Although the error in determining the extinction coefficient was much smaller than the error for K_{ip} , it was possible to directly determine the maximum

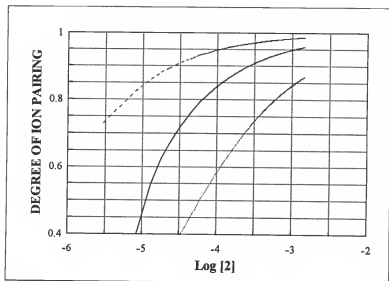


Figure 2.10. Shown above is the degree of ion-pairing for 2 as a function of three different K_{ip} 's. The K_{ip} 's that were used were as follows: 3.0×10^{-7} (dashed line); 3.0×10^{-6} (solid line, determined from Drago-Rose graph); and 3.0×10^{-5} (dotted line).

value that it could attain. A plot of absorbance/(pathlength x concentration) or $A/(b \times C)$ versus concentration over the concentration range shown above was found to plateau at concentrations above 2×10^{-3} M (Figure 2.11). The extinction coefficient was located by drawing a horizontal line across the region where the curve levelled off. For 2, a value of $180 \text{ M}^{-1}\text{cm}^{-1}$ was obtained which confirmed the value from the Drago-Rose graph (see Table 2.5).

It must be stated that although all K_{ip} 's and ϵ 's were obtained at 532 nm, this wavelength is not the absorption maximum of the charge-transfer bands for the ion-pairs. With the exception of 1, the maxima of the charge-transfer bands for the ion-pairs were in the MLCT bands. The maxima were therefore approximated by visual inspection assuming that the charge-transfer bands obey a Gaussian profile. Thus, the values of ϵ for 2 and 3 at their approximated maxima were extrapolated from the measured value at 532 nm and are shown in Table 2.5.

It was desired to determine whether the absorption data for all the ion-pairs could be applied to a Mulliken relationship (see eqn. 2.17) in which the energy of the maximum of the charge-transfer band is a function of the reduction potential of the electron acceptors. Since the oxidation potentials of Co(CO)_4^+ , the coulombic energy of attraction, and the solvent remain constant (the coulombic energy is fairly constant due to the structural similarities that exist among the ion-pairs) in the ion-pair series, a linear relationship should exist between the energy of the charge-transfer band and the reduction potential of the acceptors (see Table 2.6 for

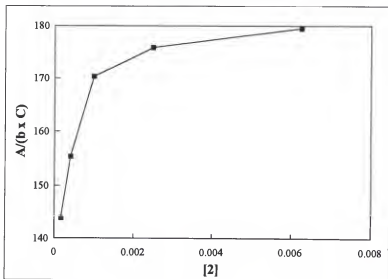


Figure 2.11. Shown above is a plot of $A/(b \times C)$ vs. $[2]$ where A = absorbance of a solution of **2** in THF, b = pathlength (1 cm) and C = molar concentration of **2** = $[2]$.

Table 2.6. Absorption charge transfer data correlation with the reduction potential of the cation component of the CT ion-pair.

Ion-pair	λ_{max} (nm)	$h\nu_{\text{CT}}$ (eV)	$E_{12}(\text{A/A}')^{\text{b}}$ (eV)
1	630	1.97	-0.63
2	525 ^a	2.36	-1.14
3	425 ^a	2.92	-1.42

a Wavelength maxima were approximated since no clearly defined maxima were identifiable.

b Reduction potentials were measured in complexes [D. Brent MacQueen and Kirk S. Schanze, *J. Am. Chem. Soc.* **1991**, 113, 7470.] possessing the same diimine ligands on the cations, but differed from these ion-pairs by possessing a N-(4-pyridyl)methyl-N,N'-dimethylaminobenzamide substituent instead of a pyridine. They are also PF_6^- salts instead of $\text{Co}(\text{CO})_4^-$ salts. The potentials are not expected to differ significantly.

the experimental data). Figure 2.12 shows the plot of $h\nu_{CT}$ versus the reduction potential, $E_{1/2}(A^+/A)$ in which (A^+/A) represents the redox couple of the electron acceptor in the ion-pair series.

Steady-State and Time-Resolved Luminescence Experiments

All steady-state and time-resolved luminescence experiments for the ion-pairs were conducted in THF, acetonitrile, or benzene at room temperature. Acetonitrile and benzene were dried over CaH_2 while THF was dried over Na/K (benzophenone was used as an indicator of dryness) and all solvents were distilled in a nitrogen atmosphere. All solutions of ion-pairs were prepared under either an argon or nitrogen atmosphere and transferred to quartz cuvettes.

In acetonitrile, excitation of all of the complexes at 355 nm resulted in fairly strong, broad, and featureless emission spectra with maxima between 580 and 600 nm. The emission has been attributed to the $d\pi(Re) \rightarrow \pi^*(diimine)$ MLCT excited state manifold [52].

At 355 nm excitation, the emission spectra of both 2 and 3 in acetonitrile strongly resembled those of 2a and 3a (see Figures 2.13 and 2.14). Note not only the similarity in shape and energy between 2 and 2a and also between 3 and 3a in acetonitrile, but the strong similarity in intensity; however, in THF, the emission spectra for the same four ion-pairs show a strong decrease of the MLCT emission.

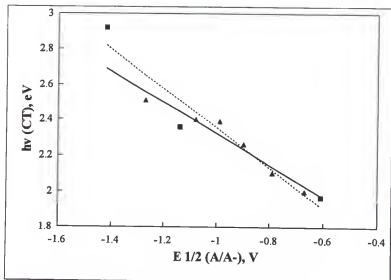


Figure 2.12. Shown above are plots of the maximum energy of the CT band, $h\nu_{CT}$, vs. the reduction potential, $E_{1/2}$ (A/A⁻), of the electron acceptor for two sets of ion-pairs which possess a common $\text{Co}(\text{CO})_4^-$ electron donor. The solid line (points are triangles; slope = -0.89 V^{-1}) is obtained from the pyridinium electron acceptors whose structures are shown in Figure 2.2, and the dashed line (points are squares; slope = -1.12 V^{-1}) is obtained from the acceptors of the present study whose structures are shown in Figure 2.6.

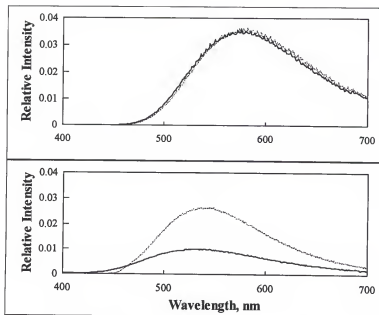


Figure 2.13. Emission spectra of 2 (solid line) and 2a (dotted line), 2a, at room temperature in CH_3CN (top) and in THF (bottom). The concentration of 2 and 2a in CH_3CN was matched to 2.5×10^{-4} , whereas in THF the concentrations of 2 and 2a were 1.6×10^{-4} and 2.0×10^{-4} , respectively.

In THF, the maximum intensity reading for the emission of solutions of **2** and **2a** with matched absorbances at 355 nm were recorded over a broad range of concentrations of **2** and are shown in Table 2.7. The relative emission intensities at 585 nm (emission maximum) were used instead of integrated emission areas in order to minimize photodecomposition of the solutions of **2**.

Excitation of both **2** and **2a** complexes ($[2] = 1 \times 10^{-4}$ M and $[2a] = 7 \times 10^{-4}$; matched absorbances at 532 nm in THF with 532 nm light gave no detectable emission.

Time-resolved emission experiments for **2** were done in THF and benzene. Tables 2.8, 2.9, and 2.10 contain the results of the experiments. For the THF and benzene data, the emission decay of **2** was fit using both single and double exponentials. For a single exponential fit, a lifetime, τ , and the goodness of fit, DW (Durbin-Watson parameter) were obtained and are reported in both tables. For a double exponential fit, two lifetimes were obtained and are reported with the normalized pre-exponential factors, α . The $\langle\tau\rangle$ values are the are the weighted averages of the τ 's obtained from the double exponential fits.

Stern-Volmer plots of the data in THF and benzene were made and quenching constants, k_q , were obtained. Tables 2.11, 2.12, and 2.13 contain all the Stern-Volmer data necessary to use in the Stern-Volmer equation, $\tau^0/\tau = 1 + k_q\tau^0[2]$, in which the charge-transfer ion-pair is itself the quencher. It was found

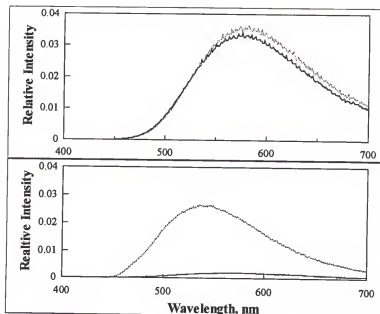


Figure 2.14. Emission spectra of **3** (whole line) and **3a** (dotted line) at room temperature in CH₃CN (top) and THF (bottom). The concentration of **3** and **3a** in CH₃CN was matched to 1.2×10^{-4} M, whereas in THF the concentrations of **3** and **3a** were 4.0×10^{-4} and 1.5×10^{-4} , respectively.

Table 2.7. Steady state emission intensity for solutions of **2** and **2a** in THF.

$[2]/M \times 10^{-6}$	Absorbance ^a	Intensity ^b (2)	Intensity (2a)	$I(2a)/I(2)^c$
5.8	0.034	5845	3773	0.6446
12	0.048	9993	14326	1.434
17	0.068	11349	25618	2.257
23	0.092	12357	31170	2.522
29	0.12	13412	38266	2.853

a Emission at 585 nm and excitation at 350 nm. The absorbance of **2a** was matched at 350 nm to that of **2**.

b Counts refers to the raw number given by the emission PMT during the experiments. 15 different counts were collected at 585 nm for **2** and **2a** and then averaged. Counts were obtained at a single wavelength (the emission maximum) instead of integrating the area of the emission over a selected wavelength range in order to reduce decomposition of the samples as a result of the excitation light.

c The ratio of the intensity of **2a** to **2**.

Table 2.8. Emission decay data for **2** in THF.

Concentration		Double exponential fit				Single exponential fit		
[2]/M $\times 10^{-6}$	α^a	τ (ns)	α^a	τ (ns)	$\langle\tau\rangle$	DW ^b	τ (ns)	DW ^b
6.6	0.79	163	0.21	9	130	1.93	131	0.87
33	0.83	111	0.17	9	94	1.97	97	1.01
66	0.85	83	0.15	9	72	2.19	75	1.41
330	0.81	31	0.19	7	26	1.86	29	0.87
660	0.77	20	0.23	5	17	2.05	19	1.21

τ^o **2a** in THF = 233.5 ns

a Normalized pre-exponential factors.

b Durbin-Watson (DW) parameter which measures the goodness of fit; typically, values ≥ 1.60 indicate a satisfactory fit.

Table 2.9. Emission decay for 2 in benzene.

Concentration		Double exponential fit				Single exponential fit		
[2]/M x 10 ⁻⁶	α_1	τ_1	α_2 (ns)	τ_2	$\langle\tau\rangle$ (ns)	DW (ns)	τ (ns)	DW
13	0.44	9.2	0.56	104.5	62.3	1.40	81.7	0.31
90	0.49	28.7	0.51	134.4	82.6	1.99	77.6	0.76
130	0.41	15.2	0.59	65.7	45.0	1.64	51.0	0.45
180	0.57	36.7	0.43	181.7	99.1	2.02	82.8	1.07
360	0.60	33.5	0.40	126.1	70.5	2.11	64.9	1.10
900	0.69	29.6	0.31	53.0	36.9	1.86	37.6	1.57

τ^O 2a in benzene = 420.8 ns

Table 2.10. Emission decay data for **2** in CH₃CN.

[2]/M ($\times 10^{-6}$)	τ ns	DW
150	205.1	1.75
750	138.3	2.01
1500	100.1	1.96
7500	31.0	1.81
15000	16.9	1.77

τ^0 (**2a**) = 224 ns in CH₃CN.

The correlation coefficient for the Stern-Volmer plot of the above data was 0.9998; k_q was calculated to be $3.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

Table 2.11. Stern-Volmer Data for **2** in THF at room temperature.

$[2]/M$ $\times 10^{-6}$	τ (ns)	τ^0/τ
6.6	131	1.79
33	97	2.40
66	75	3.11
330	29	7.94
660	19	12.49

τ^0 (**2a**) = 237 ns in THF.

The correlation coefficient for the Stern-Volmer plot of the above data is 0.994. k_q was calculated to be $7.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$.

Table 2.12. Stern-Volmer Data for **2** in benzene at room temperature.

$[2]/M$ $\times 10^{-6}$	τ (ns)	τ^0/τ
13	62.3	6.75
90	82.6	2.40
130	45.0	9.35
180	99.1	4.25
360	36.9	11.40

τ^0 (**2a**) = 421 ns in benzene.

The correlation coefficient for the Stern-Volmer plot of the above data was very low (< 0.10).

Table 2.13. Stern-Volmer data for **2** in CH_3CN at room temperature.

$[2]/M$ $\times 10^{-6}$	τ (ns)	τ^0/τ
150	205.1	1.09
750	138.3	1.62
1500	100.1	2.24
7500	31.3	7.23
15000	16.9	13.25

τ^0 (**2a**) = 224 in CH_3CN .

a The correlation coefficient for the Stern-Volmer plot of the above data is 1.000; k_q was calculated to be $3.6 \times 10^{10} \text{ M}^{-1}\text{cm}^{-1}$.

that the lifetimes for **2** in benzene did not consistently decrease over an increasing concentration range of **2** as previously observed in THF (See Table 2.8). The lifetime data in benzene for **2** could not fit the Stern-Volmer equation shown above and therefore, a k_q could not be obtained. The lifetimes for the various concentrations of **2** in benzene shown in Table 2.9 appeared to remain relatively constant.

Stern-Volmer plots were generated for both the time-resolved and steady-state luminescence data of **2** in THF and are shown in Figure 2.15. The plots were generated from k_q values of 7×10^{10} and $4 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$ obtained from the time-resolved and steady-state data, respectively. Figure 2.15 shows the Stern-Volmer fit of the steady state data from Table 2.7 (squares) and the lifetime data (single exponentials) from Table 2.11 (diamonds). In addition to the two Stern-Volmer plots generated from experimental data, another Stern-Volmer plot was developed using Debye-Huckel Theory (solid line).

The maximum theoretical diffusion-controlled reaction rate from Debye-Huckel Theory, k_q^{DH} , was obtained by using the following equation [54]:

$$k_q^{\text{DH}} = (2kT/3\eta)(R_{\text{Re}}+R_{\text{Co}})^2(1/R_{\text{Re}}R_{\text{Co}})(S/(e^S-1)) \quad (2-23)$$

where S is the following:

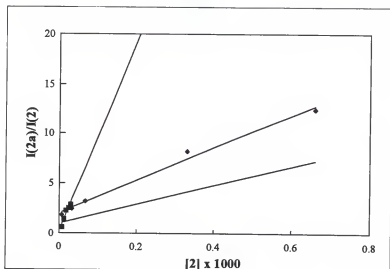


Figure 2.15. Shown above are Stern-Volmer plots generated for 2 in THF. The top plot (squares) was generated using a $k_q = 4 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$ obtained from the steady-state data for 2 in THF shown in Table 2.7. The middle plot (diamonds) was generated using a $k_q = 7 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$ obtained from single exponential time-resolved data in Table 2.11. The bottom plot (solid line) was generated using a $k_q = 4 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$ obtained from Debye-Huckel theory.

$$S = (z^{Re} z^{Co} e^2) / (4\pi\epsilon_0\epsilon D_{ReCo} kT) \quad (2-24)$$

and the variables are defined as follows: k is the Boltzmann constant (1.38×10^{23} J/K), T is the temperature (298 K), η is the viscosity of the solvent ($\eta_{THF} = 5.5 \times 10^4$ N/m²s), R_{Re} and R_{Co} are the radii in angstroms, for the cation and anion of the ion-pair, respectively, z is the formal charge of the ions ($z^{Re} = 1$, $z^{Co} = -1$), ϵ_0 is the permittivity of space (8.85×10^{-12} C²/Nm²), ϵ is the dielectric constant of the solvent ($\epsilon_{THF} = 7.6$), and D_{ReCo} is the distance at which the ET event occurs.

In order to carry out the calculation for k_q^{DH} , the radii of the ions and the interatomic distance over which electron transfer occurs were needed. The radii were estimated to be 4.15 Å for the cation, Re, and 4.73 Å for the anion, Co. The distance over which they engage in electron transfer was 3.3 Å which was obtained from x-ray crystallographic data.

X-ray Crystallographic Data

An x-ray structure was obtained for **2** and all crystallographic parameters are contained in the Appendix. Figure 2.16 shows the the unit cell and Figures 2.17 and 2.18 show the two *different* ion-pairs in the unit cell. Notice that in the first packing structure, **2**, the anion lies directly below the bipyridine ligand of the cation. From the x-ray coordinates, one of the carbonyl oxygens of the anion, O4, lies 3.263 Å from one of the nitrogens, N2, of the bipyridyl ring and another

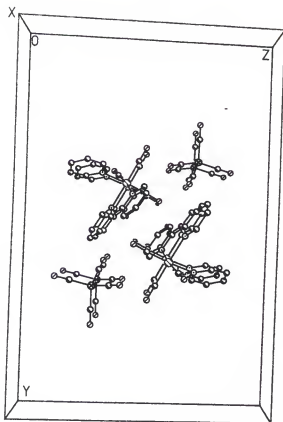


Figure 2.16. A representation of the unit cell for ion-pair 2.

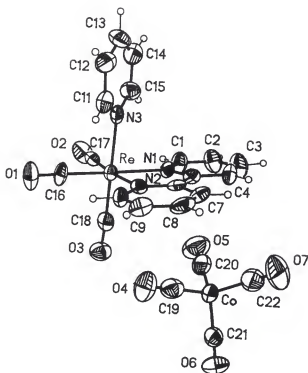


Figure 2.17. ORTEP diagram of the ion-pair believed to engage in CT for **2**. The relevant CT interaction is shown between the tetracarbonylcobaltate and the bipyridine ligand of the cation. Referred to in the text as **2**.

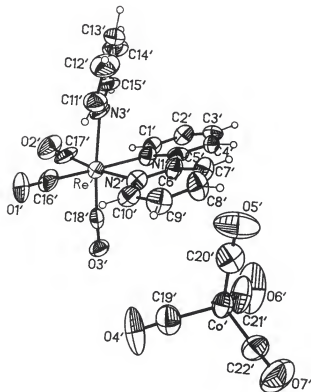


Figure 2.18. ORTEP diagram of the second ion-pair which is believed not to engage in CT for **2**. Referred to in the text as **2'**.

carbonyl oxygen, O5, lies 3.319 Å from the other nitrogen, N1, of the ring. The O4-N2 and O5-N1 distances are the shortest intermolecular distances present in ion-pair 2.

In the second ion-pair, 2', the anion is on the same equatorial side of the cation, except it is not located below the bipyridine, but away from it. In ion-pair 2', O5 lies approximately in the aromatic plane of the pyridine, but it is not underneath it.

A selected comparison of the bond lengths and bond angles of the cation of both ion-pairs 2 and 2' with those appertaining to cation 4 (a similar cation) is shown in Table 2.14 [55]. All bond lengths and bond angles for the anion of both ion-pairs 2 and 2' are also displayed in Table 2.14.

IR Spectroscopy

IR spectra of 2, 3, 2a, and 3a were obtained in both the solid and liquid phases. Table 2.15 contains the IR spectral data for all four complexes as well as literature values for the tetracarbonyl cobaltate ion of several other similar ion-pairs. All solid phase IR spectra were obtained in 0.1 % m/m KBr disks whereas liquid phase spectra were obtained in neat THF solutions having concentrations of 0.5 to 1 mM. The solid and solution phase IR spectra for 2, 2a and 3, 3a are shown in Figure 2.19 and 2.20, respectively.

Table 2.14. Selected bond lengths and bond angles for heavy atoms in 2, 2', and 4 [55]. 2 and 2' are the designations for the two ion-pairs found in the unit cell.

1	2	3	1-2(2) (Å)	1-2(2') (Å)	1-2(4) (Å)	1-2-3(2) (°)	1-2-3(2') (°)	1-2-3(4) (°)	—
N1	Re	N2	2.177(13)	2.156(13)	2.11(1)	75.0(5)	75.9(5)	73.6(5)	
N2	Re	N3	2.185(13)	2.169(13)	2.16(1)	85.4(5)	81.3(5)	85.1(4)	
C16	Re	C17	1.93(2)	1.98(2)	1.80(2)	87.8(7)	87.2(8)	81.7(8)	
C17	Re	C18	1.94(2)	1.90(2)	1.81(2)	90.2(8)	89.4(8)	88.5(7)	
C1	N1	C5	1.34(2)	1.35(2)	1.35(1)	119.7(14)	117.2(4)	N/A	
C5	N1	Re	1.37(2)	1.36(2)	1.36(1)	115.0(10)	N/A	N/A	
C6	N2	C10	1.34(2)	1.38(2)	1.27(1)	120.7(14)	119.4(14)	N/A	
C10	N2	Re	1.33(2)	1.35(2)	1.37(2)	123.0(11)	N/A	N/A	
C19	Co	C20	1.75(3)	1.78(2)	-	107.0(11)	112.5(10)	-	
C19	Co	C21				113.5(10)	108.4(10)	-	
C20	Co	C21	1.75(2)	1.73(2)	-	106.3(11)	107.4(10)	-	
C20	Co	C22				108.3(11)	109.5(10)	-	
C21	Co	C22	1.74(2)	1.78(2)	-	110.7(11)	107.0(10)	-	
C22	Co	C19	1.79(3)	1.76(2)	-	110.6(12)	111.7(10)	-	
C19	O4		1.16(3)	1.11(3)	-				
C20	O5		1.15(3)	1.17(3)	-				
C21	O6		1.15(3)	1.12(3)	-				
C22	O7		1.08(4)	1.12(3)	-				

Table 2.15. Solid-state and solution IR spectra of 3, 3a, 2 and 2a.

3a	3	2a	2	[NCP ⁺ , Co(CO) ₄] ⁺	[Na ⁺ , Co(CO) ₄] ⁺
2032 (2033)	2033 (2031)	2033 (2030)	2036 (2033) 2001 (2019)	2006 (2003) 1911 (1916)	2025 (2007) 1935 (1910)
1948 (1951)	1947 (1948)	1929 (1927)	1988 (2002) 1922 (1926)		
1922 (1925)	1924 (1922)	1903	1923		
	1877 (1876)		1880 (1886)	1878 (1886) 1865 (1870)	1868 (1853)

Note: ν_{CO} values in cm^{-1} for solid state spectra (0.1 - 0.5 %) in KBr disk. Values for THF are given in parantheses (0.5 - 1.0 mM).

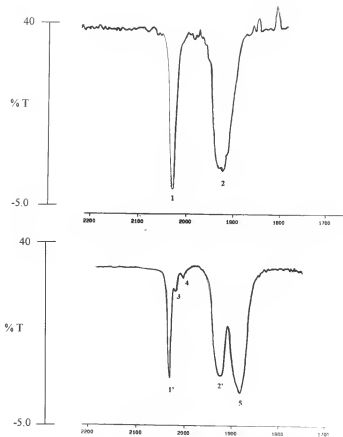


Figure 2.19. IR spectra for 2a (top) and 2 (bottom) as solutions in THF. The concentration of 2a was 3.2×10^{-4} M, while the concentration of 2 was 5.0×10^{-3} M. The peaks marked 1 and 2 for ion-pair 2a correspond to 2030 and 1927 cm^{-1} , respectively. Peaks 1', 2', 3, 4, and 5 correspond to 2033, 1926, 2019, 2002, and 1886 cm^{-1} , respectively.

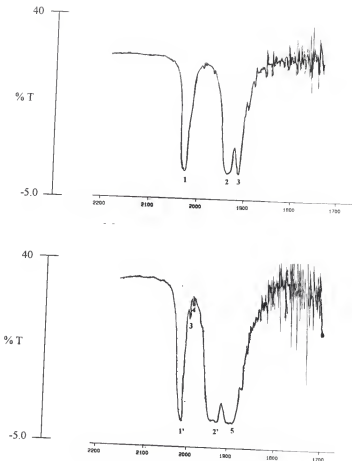


Figure 2.20. IR spectra above for **2a** (top) and **2** (bottom) in KBr. The concentration of **2a** was 0.81 % m/m, while the concentration of **2** was 1.4 % m/m. The peaks marked 1, 2, and 3 for ion-pair **2a** correspond to 2033, 1929, and 1903 cm^{-1} , respectively. Peaks 1', 2', 3, 4, and 5 correspond to 2026, 1922, 2001, 1988, and 1880 cm^{-1} , respectively.

Transient-Absorption (TA) Spectroscopy

Transient absorption (TA) spectroscopy was done using a flash photolysis apparatus which has been previously described [56]. All work was done using a 100 mL circulating cell since it provided fresh volumes of solution to the laser pulse. Typically, 5-10 mJ pulses were used and the decay traces were visualized on a very short time-scale window (500 ns total).

In the following section, the calculation of the difference extinction coefficient, $\Delta\epsilon$, of **2a** in acetonitrile will be outlined. **2a** was used as an actinometer throughout the transient absorption experiments in order to calculate the yield of cage escape products derived from electron transfer quenching of the excited state (See equilibrium of **5** $\rightarrow$ **6** in Figure 2.6) to that of the total concentration of excited states (Excited cation is shown in **3** and **4** of Figure 2.6). It was assumed that the total concentration of excited state species calculated for **2a** would be the same for the cations of the other two charge-transfer ion-pairs.

Calculation of the difference extinction coefficient, $\Delta\epsilon$, for the excited state of **2a**

A difference extinction coefficient, $\Delta\epsilon$, for the absorption of the excited triplet MLCT state of **2a** at 370 nm was obtained as follows: the absorbances of acetonitrile solutions of **2a** and benzophenone (**BP**) were matched at 356 nm ($A = 0.2$). The solutions were placed in quartz cuvettes, argon-degassed, and the

absorbances were re-checked. Difference absorbances (ΔA_s) were obtained at 370 nm for **2a** and 520 nm for **BP**, the respective wavelengths of maximum transient absorption for each compound, over a range of laser powers and a plot of ΔA_{BP} vs ΔA_{2a} is shown in Figure 2.21.

In order to obtain the $\Delta \epsilon$ at 370 nm for the excited state of **2a**, the transient absorbance form of the Beer-Lambert equation for **BP** ($\Delta A_{BP} = \Delta \epsilon_{BP} b C$) was divided by the same respective equation for **2a** ($\Delta A_{2a} = \Delta \epsilon_{2a} b C$):

$$\Delta A_{BP} / \Delta A_{2a} = \Delta \epsilon_{BP} / \Delta \epsilon_{2a} \quad (2-25)$$

and since the slope of the line, m , in Figure 2.21 is equal to $\Delta A_{BP} / \Delta A_{2a}$, the following holds true for $\Delta \epsilon_{2a}$

$$\Delta \epsilon_{2a} = \Delta \epsilon_{BP} / m \quad (2-26)$$

in which the triplet-triplet $\Delta \epsilon_{BP}$ at 520 nm = $6500 \pm 400 \text{ M}^{-1} \text{ cm}^{-1}$ [57], $m = 0.546$ from Figure 2.21 (the correlation coefficient of the plot was 0.990), and $\Delta \epsilon_{2a}$ was calculated to be $1.19 \times 10^4 \pm 700 \text{ M}^{-1} \text{ cm}^{-1}$.

From a knowledge of $\Delta \epsilon_{2a}$, it is possible to ascertain the concentration, C , of excited state species of the cation, Re^+ , if its ΔA is known (using the Beer-Lambert equation). If electron transfer quenching of the excited is achieved with

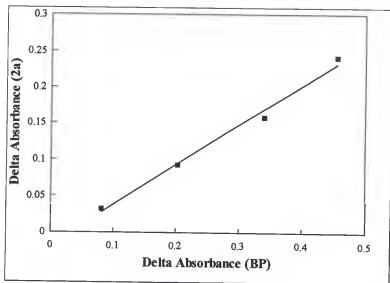


Figure 2.21. A plot of Delta Absorbance of BP at 520 nm versus Delta Absorbance of 2a at 370 nm (both in CH_3CN) as a function of laser power. The absorbances of both solutions were matched at 355 nm. The correlation coefficient was 0.990.

unit efficiency, then the total concentration of the quenched excited state of Re is known (the same as the excited state concentration). As a result of electron transfer quenching of the excited state of Re, radicals of Re are generated in the ion-pair solvent cage. In the next section, the calculation of the yield of Re radicals which have escaped the solvent cage will be elaborated.

Calculation of the cage escape yields for the 2a/DABCO (diazabicyclooctane) system

From the sequence of events shown in Figure 2.22, the concentration of free Re radicals generated by the electron transfer quenching of the excited state of Re by diazabicyclooctane (DABCO) may be calculated. In order to quench > 99% of the MLCT excited states of 2a (1.0×10^{-4} M in CH_3CN), a concentration of 0.05 M DABCO was required. The concentration was calculated from the Stern-Volmer equation using an experimentally determined value of $9.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for the second-order quenching of Re cation by DABCO.*

The MLCT state of 2a was obtained by irradiating a solution of 2a with 355 nm light. The excited state is quenched by forward electron transfer from

* The concentration of DABCO needed to quench > 99% of the excited states of Re was calculated by the Stern-Volmer (S-V) equation: $\tau^0/\tau = 1 + k_q\tau^0[\text{DABCO}]$. Since k_q was determined to be $9.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, and τ^0 (the lifetime of 2a without quencher present) = 224 ns, only the ratio of τ^0/τ was needed to obtain [DABCO]. The formula for the quantum yield for quenching, Φ , is $\Phi = 1 - \tau/\tau^0$. A value of Φ necessary to quench > 99 % of the excited states of Re would indicate that the resultant emission lifetime is 2.2 ns. The ratio, τ^0/τ for the S-V equation is thus 224 ns/2.2 ns or 102.

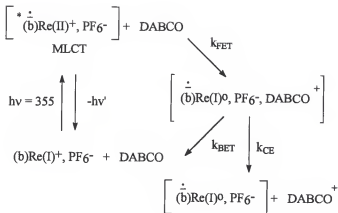


Figure 2.22. Sequence of events initiated by the absorption of 355 nm light to populate the MLCT excited state of the cation, $(b)\text{Re(I)}^+$. Quenching of the MLCT state by DABCO leads to a radical ion-pair that can either undergo back electron transfer (BET) or cage escape (CE) to yield the free ions.

DABCO to produce a reduced Re and the DABCO radical cation. The geminate radical ion-pair may either recombine to return to the ground state or may dissociate in solution to yield free reduced Re and DABCO radical cations.

Paraquat (an electron scavenger) dication was present in appreciable enough concentration (5×10^{-4} M) to scavenge all of the free reduced Re cation in solution (the concentration of free reduced Re is typically 4×10^{-6} M at laser powers of 10 mJ). Paraquat scavenges the electron from the free reduced Re to generate a paraquat monocation. From the difference extinction coefficient of the paraquat monocation (at 605 nm, $\Delta\epsilon = 10,060 \text{ M}^{-1}\text{cm}^{-1}$) [58], the concentration of free reduced Re may be determined since the absorption signal arising from the reduced paraquat is due to the free reduced Re that has been scavenged.

The equations necessary to obtain the quantum yield of free reduced Re is shown below: first, the concentration of the excited state of an acetonitrile solution of **2a** was calculated by obtaining ΔA from transient absorption experiments at 370 nm and using the Beer-Lambert equation

$$C_{\text{Re}} = \Delta A_{370} / (\Delta\epsilon_{370} \times b) \quad (2-27)$$

in which C_{Re} = concentration of excited state species, $\Delta\epsilon_{370}$ from previous calculations = $11,900 \text{ M}^{-1}\text{cm}^{-1}$, and b is the path length. The concentration of reduced paraquat was likewise obtained by dividing its ΔA at 605 nm by $\Delta\epsilon_{605}$:

$$C_{PQ} = \Delta A_{605} / \Delta \epsilon_{605} \quad (2-28)$$

Since the concentration of the paraquat monocation is equal to free reduced Re formed by photoinduced electron transfer from DABCO followed by cage escape, the quantum yield for free reduced Re, Φ_{CE} , was obtained by dividing the concentration of paraquat monocation by the concentration of excited state Re:

$$\Phi_{CE} = C_{PQ} / C_{\bullet Re} \quad (2-29).$$

If the concentration of reduced Re that escapes from the geminate radical ion-pair is known, then it is possible to obtain a difference extinction coefficient, $\Delta \epsilon$, for it. Once the difference extinction coefficient for the reduced Re is known, the concentration of free reduced Re may be determined. The method used to obtain $\Delta \epsilon$ for the reduced Re is described in the next section.

Calculation of the difference extinction coefficients, $\Delta \epsilon$, for reduced Re in 2a and 3a

The difference extinction coefficient, $\Delta \epsilon$, was determined for reduced Re in 2a and 3a as follows: the total concentration of free reduced Re, C_{Q-Re} , from electron transfer quenching of the excited state of Re was obtained by multiplying

the quantum yield for cage escape, Φ_{CE} , by the concentration of excited state species, C_{Re} , assuming total quenching of the excited state:

$$C_{Q-Re} = \Phi_{CE} * C_{Re} \quad (2-30)$$

$\Delta\epsilon$ for reduced Re, $\Delta\epsilon_{Red-Re}$ was calculated by obtaining ΔA for the free reduced Re at either 350 or 490 nm (the local maxima in the transient absorption spectrum for the absorption of reduced Re; see Figure 2.23 for transient absorption spectrum of reduced Re) and using the following equation:

$$\Delta\epsilon_{Q-Re} = \Delta A / (b \times C_{Q-Re}) \quad (2-31)$$

The calculated values for $\Delta\epsilon_{Q-Re}$ at both 350 and 490 nm are shown in the Table 2.16.

Finally, the calculation of the quantum yield for the free reduced Re of the charge-transfer ion-pairs is described in the next section.

Calculation of quantum yields for cage escape of the reduced Re of the charge-transfer ion-pairs

The calculation of the quantum yield for free reduced Re of the charge-transfer ion-pairs was done at both 355 and 532 nm excitation. The calculations at

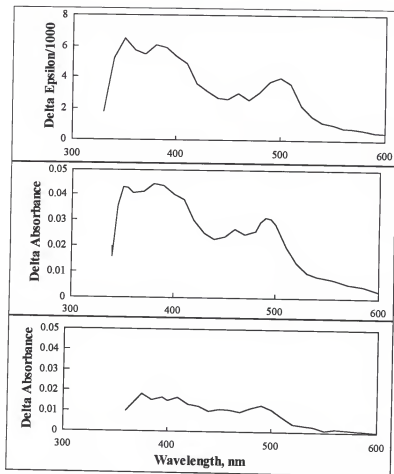


Figure 2.23. The top figure is the extinction coefficient spectrum of reduced 2a generated from a THF solution of 2a (Absorbance at 355 = 0.3) and 0.05 M triethylamine. The middle spectrum was generated from a 0.1 mM solution of 2 in THF irradiated at 355 nm with a laser power of 10 mJ. Both spectra were obtained at 40 μ s delay time. The lowest spectrum was generated from a 1 mM solution of 2 in THF irradiated at 532 nm at a laser power of 40 mJ. It was obtained at 0 μ s delay time.

Table 2.16. The difference extinction coefficients, $\Delta\epsilon$, calculated for the reduced forms of **2a** and **3a** at both 350 and 490 nm.

Ion-Pair	$\Delta\epsilon_{350}$ ($M^{-1}cm^{-1}$)	$\Delta\epsilon_{490}$ ($M^{-1}cm^{-1}$)
2a	6500	3700
3a	7000	3700

the two excitation wavelengths differ from each other and will be treated separately. For 355 nm excitation, the absorbances of a THF solution of **2** and an acetonitrile solution of **2a** were matched at 355 nm ($A \approx 0.2 - 0.3$). ΔA 's were obtained for free reduced Re of **2** at 350 nm and for the excited state of **2a** at 370 nm. The concentrations of the excited states, C_{*Re} , and free reduced Re, C_{Q-Re} , were calculated using equations (2-27) and (2-30), respectively. The quantum yield for the cage escape of reduced Re in **2** or **3** is thus equal to:

$$\Phi_{CE} = C_{Q-Re}/C_{*Re} \quad (2-32)$$

A visible actinometer with a fairly strong extinction coefficient at 532 nm was needed to carry out the calculations of the quantum yield for free reduced Re of **2** or **3** upon excitation with 532 nm light. Unfortunately, **2a** could not be used as the visible actinometer since its extinction coefficient at 532 nm is less than $35 \text{ M}^{-1}\text{cm}^{-1}$ and the preparation of actinometric solutions of **2a** would require a prohibitively large concentration of **2** (about 0.01 M). A concentration of 0.01 M would not allow the absorbance of the excited state at 370 nm to be monitored because the transmittance at this wavelength would be very low (since $\epsilon \approx 3000 \text{ M}^{-1}\text{cm}^{-1}$ at 355 nm). $[\text{Ru}(\text{bpy})_3]^{+2}$, $(\text{Cl}^-)_2$ (hereafter referred to as *Ru*) in water was chosen as the actinometer it has a strong triplet MLCT absorption in the visible region of the spectrum ($\lambda_{\text{max}} = 450 \text{ nm}$). It was decided

that the difference absorbance (ΔA) at 370 nm would be used to monitor the MLCT excited state concentration for Ru. 370 nm was chosen since the ground state absorbance was measured to be 1.15 (the lowest absorbance in the UV-vis region) in relation to an absorbance of 0.22 at 532 nm (the excitation wavelength). Although the transmittance is only 7% at 370, good signals are nonetheless obtained because of the good response provided by the TA detection.

It was necessary to obtain a value for the extinction coefficient at 370 nm for the excited state of Ru. Prior to determining the extinction coefficient, it was necessary to determine whether the response of the absorbance of Ru was linear with respect to laser power. Figure 2.24 shows that a plot of the difference absorbance (ΔA) of Ru in water versus laser power is linear up to 40 mJ laser pulses. The $\Delta \epsilon$ at 370 was thus calculated by using the following equation:

$$\Delta \epsilon_{370} = (\Delta A_{370} / \Delta A_{450}) \Delta \epsilon_{450} \quad (2-33)$$

in which $\Delta \epsilon_{450} = -7600 \text{ M}^{-1}\text{cm}^{-1}$ (the value is negative because of ground state bleaching) [59]. The ratio of the difference absorbances at 370 and 450 of Ru was obtained and multiplied by $-7600 \text{ M}^{-1}\text{cm}^{-1}$ to give $\Delta \epsilon_{370}$. The latter step was repeated in triplicate, the values inserted into eqn. 2-33, and a value of $1.21 \times 10^4 \pm 300 \text{ M}^{-1}\text{cm}^{-1}$ for $\Delta \epsilon_{450}$ was obtained.

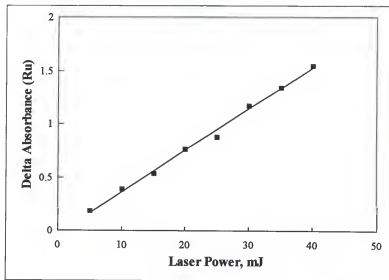


Figure 2.24. A plot of Delta Absorbance of a solution of Ru [5.0×10^{-5}] in water at 370 nm as a function of the laser power at an excitation wavelength of 355 nm. The correlation coefficient was 0.995.

Solutions of the actinometer, Ru, in water and 2 or 3 in THF were prepared with absorbances at 532 nm = 0.20, irradiated at 532 nm excitation, and ΔA 's were obtained at 370 and 350 nm, respectively. The concentration of excited state species, C_{Ru} , was determined by the following equation:

$$C_{Ru} = \Delta A_{370} / (b \times \Delta \epsilon_{370}) \quad (2-34)$$

in which ΔA_{370} is a measured value, b is the pathlength, and $\Delta \epsilon_{370}$ was calculated value (see above). The total concentration of free reduced Re, C_{Q-Re} was determined by applying the measured value of ΔA_{370} into a rearranged form of eqn. (2-31). The quantum yield for free reduced Re, Φ_{CE}' , at 532 nm excitation was given by the following equation (see also eqn. 2-32 and preceding discussion to the equation.):

$$\Phi_{CE}' = C_{Q-Re} / C_{Ru} \quad (2-35)$$

TA experiments were the crux of the work done with the ion-pairs. The purpose of the TA experiments was to determine the difference in efficiencies of the yield of free Re from 355 nm (MLCT band) versus 532 nm (charge-transfer band) excitation. All pathways available to the ion-pair as a result of photoexcitation are shown in Figure 2.6. As evident in the figure, all pathways

terminate in the dissociation of the geminate radical ion-pair to free Re and free Co (5 → 6). The most important aspect of this study was to determine if any measurable difference existed in the efficiency of cage escape from 5 by accessing it either from MLCT excitation (4 → 5) or from CT excitation (2 → 5). Cage escape yields of reduced Re for **2** and **3** were measured in THF as described above (*vide supra*). At 355 nm excitation, solutions of charge-transfer ion-pairs were typically 1×10^{-4} M whereas at 532 nm excitation, the concentrations were generally 1×10^{-3} M. Results of the cage escape from 5 (Figure 2.5) as accessed by the two different excitation wavelengths are recorded in Table 2.17 for **2** and **3**.

A TA spectrum for the reduced form of **2a** in acetonitrile is shown in Figure 2.23. The solution of **2a** had an absorbance of 0.2 at 355 nm and a concentration of 0.05 M triethylamine in order to quench > 97 % of the MLCT excited states. The spectrum shown was obtained at a time = 0 ns using a laser pulse of 5 mJ. Note the two signature peaks at 350 and 490 nm for the reduced Re. Figure 2.20 shows the spectrum of **2** in THF at a concentration of 1.5×10^{-4} M at 355 nm excitation. The intensity and shape of the peaks at 350 and 490 nm confirm that it is due to the absorption of reduced Re. The same TA spectrum for **2** in THF at 1.0×10^{-3} M was obtained at 532 nm excitation and is shown in Figure 2.23; however, as observed, its intensity was much less (by a factor of 5) than the spectrum obtained at 355 nm. Prior to cage escape experiments, the linearity of the difference absorbance of **2** was evaluated as a function of laser power at 355 and

Table 2.17. Quantum yields of free reduced cations in THF after application of 355 and 532 nm wavelengths.

Ion-pair	$\Phi(355\text{ nm})^a$	$\Phi(532\text{ nm})^b$
1	N/A	N/A
2	0.65	0.040
3	0.67	0.036
$[\text{Q}^+, \text{Co}(\text{CO})_4]$	0.04	0.007

a Φ refers to the quantum yield of free reduced cations. The experiments were done at 10 mJ laser power.

b The experiments were done at 40 mJ laser power except for $[\text{Q}^+, \text{Co}(\text{CO})_4]$ which was done at 10 mJ power.

532 nm. Figure 2.25 and 2.26 show the results of the linearity experiments. The linearity begins to deviate at a laser power of 20 mJ for both excitation wavelengths (more evident for linearity experiment with excitation laser wavelength of 355 nm).

The cage escape yields for the $[Q^+, Co(Co)_4]$ ion-pair at 355 and 532 nm excitation wavelengths was also determined. The absorption spectra of $[Q^+, PF_6^-]$ and $[Q^+, Co(Co)_4]$ in THF are displayed in Figure 2.27. $[Q^+, Co(Co)_4]$ has a charge-transfer absorption at a maximum wavelength of 560 nm, whereas $[Q^+, PF_6^-]$ does not absorb in the visible.

$[Q^+, Co(Co)_4]$ was irradiated at a concentration of 1.0×10^{-3} M at both 355 and 532 nm absorption. The free reduced cation had a single transient absorption maximum in THF at 505 nm. In order to determine the cage escape yield of the reduced cation from the two excitation wavelengths, it was necessary to first obtain the difference extinction coefficient of the reduced cation at 505 nm. The difference coefficient can be used to obtain the concentration (C) from the Beer-Lambert equation, $C = \Delta A / \Delta \epsilon b$.

The excited cation was initially generated by the application of 355 nm to a 5.0×10^{-3} M solution of $[Q^+, PF_6^-]$. The excited cation was completely quenched by electron transfer from biphenyl (1.0×10^{-1} M) to generate the reduced cation ($Q^\cdot$) and the oxidized biphenyl cation ($BP^{+\cdot}$). Since the oxidized biphenyl cation had a difference coefficient of 1.45×10^4 M⁻¹cm⁻¹ at 670 nm (the maximum

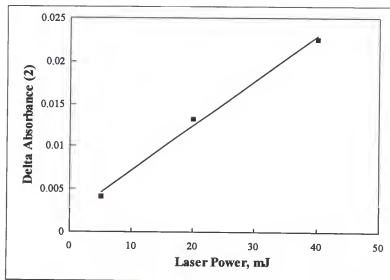


Figure 2.25. Delta Absorbance of a solution of **2** [1.0×10^{-3}] in THF at 350 nm as a function of the laser power at an excitation wavelength of 532 nm. The correlation coefficient was 0.994.

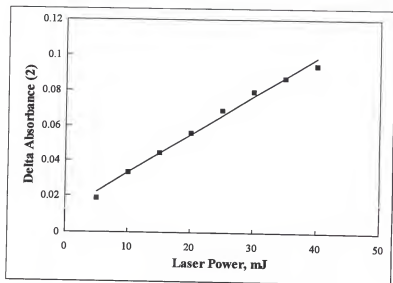


Figure 2.26. Delta Absorbance of a solution of **2** [1.2×10^{-4}] in THF at 350 nm as a function of the laser power at an excitation wavelength of 355 nm. Each point is the average of three trials. The correlation coefficient was 0.991.

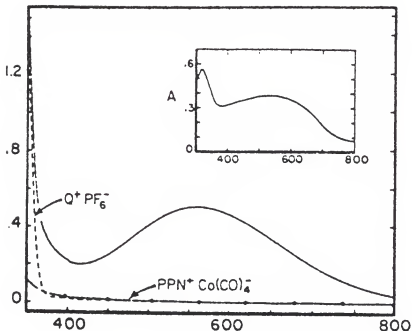


Figure 2.27. Charge-transfer absorption spectra of $[Q^+, Co(CO)_4^-]$ at a concentration of $1 \times 10^{-3} M$ in CH_2Cl_2 together with the absorption spectra of the separate cation acceptor, $[Q^+, PF_6^-]$, and the anion, $[PPN^+, Co(CO)_4^-]$. The diffuse reflectance spectrum of the corresponding crystalline salt as a 10% dispersion in silica is shown in the inset.

wavelength of transient absorption) [60], the ratio of the difference absorbances for Q[•] (505 nm) and BP^{•+} (670 nm), $\Delta A_{505}/\Delta A_{670}$, may be used to calculate the difference extinction, $\Delta \epsilon_{505}$, for Q[•]. The following equation was used to obtain $\Delta \epsilon_{505}$ for Q[•]:

$$\Delta \epsilon_{505} = (\Delta A_{505}/\Delta A_{670})(1.45 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}) \quad (2-36)$$

The ratio, $\Delta A_{505}/\Delta A_{670}$, was obtained for several different solutions of [Q[•], PF₆⁻] and BP and the value obtained for $\Delta \epsilon_{505}$ was $2.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$. $2.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ was the value used in the Beer-Lambert equation to obtain the concentrations of Q[•] after 355 and 532 nm excitation of separate $1.0 \times 10^{-3} \text{ M}$ solutions of [Q[•], Co(CO)₄]⁻ in THF.

Discussion

Evidence of Charge-Transfer Interaction in the Charge-Transfer Ion-Pairs

The work has focused on the preparation of charge-transfer ion-pairs that possess in addition to an MLCT absorption band, a charge-transfer absorption band. Ion-pairs 1, 2, and 3 (shown in Figure 2.5) are structurally similar and differ only in the reduction potential of the electron acceptor (the cation). Thus, the energy of any charge-transfer band that is observed in the electronic spectra of the

ion-pairs should differ in a manner consistent with the electron affinity of the acceptor. *Prima facie* evidence for the existence of a ground state charge-transfer interaction has been obtained by the electronic absorption spectra, x-ray crystallography, IR spectra, and luminescence experiments.

Upon the precipitation of 1, 2, and 3, out of water, it is readily apparent that their colors do not resemble those of the starting materials. Specifically, 1a is orange while 1 is orange-red, 2a is yellow while 2 is dark red, and 3a is red-yellow while 3 is red-orange. These experimental observations provided strong preliminary evidence for the existence of charge-transfer interactions in the ion-pairs.

Electronic absorption spectra of solutions of the charge-transfer ion-pairs support the preliminary color observation by demonstrating that a weak absorption band appears in visible region of the spectrum for 1, 2, and 3. Although the low-energy bands are relatively weak for 1, 2, and 3 ranging from $120 \text{ M}^{-1}\text{cm}^{-1}$ for 3 to $320 \text{ M}^{-1}\text{cm}^{-1}$, they are not found in the absorbance spectra for 1a, 2a, or 3a.

The charge-transfer band is fairly broad and featureless and is approximately 5000 cm^{-1} at fwhm. The intensity, shape, and energy of the charge-transfer bands for 1, 2, and 3 are typical for weak charge-transfer complexes [61]. In fact, the similarity between the charge-transfer bands of 2 and $[\text{PP}^+, \text{Co}(\text{CO})_4^-]$ (see Table 2.2 in *Introduction*) is very striking. A reasonable comparison may be made between the two since the *bpy* ligand of the cation (see below for

examination of the x-ray structure of **2**) is structurally similar to PP^+ . In fact, the reduction potentials of the two cations differ by only about 100 mV. Notice that the maximum for each charge-transfer band is located at about 500 nm, while the intensities are roughly similar (230 vs 380 $M^{-1}cm^{-1}$, for **2** and $[PP^+, Co(CO)_4]^-$, respectively).

Further support for a charge-transfer interaction in **1**, **2**, and **3** was obtained by x-ray crystallography and IR spectra. An x-ray structure was obtained for **2** and illustrated a unit cells containing two different ion-pairs (See Figures 16-18 for ion-pairs and unit cell structure). One of the ion-pairs, **2**, showed that carbonyl oxygens O5 and O4 of the anion were 3.263 Å and 3.319 Å from the two diimine nitrogens, N1 and N2, respectively, of the cation. The distances were within the van der Waals radii of the respective atoms and are therefore believed to be potential routes for charge-transfer interaction. For ion-pair **2'**, no interaction sites presented themselves as likely candidates for charge-transfer. It was speculated that charge-transfer is occurring in only one of the ion-pairs present in the unit cell. In Table 2.14, some of the more relevant bond distances and bond angles are presented for both **2** and **2'** and are compared to **4**, a compound structurally similar to the cation of **2**, although possessing PF_6^- counterions instead of $Co(CO)_4^-$. It is readily apparent that a charge-transfer interaction does not ostensibly perturb the bond distances found in the cation of ion-pair **2**. Both ion-pair **2** and **2'** display bond lengths that do not differ too much from each other or from **4**. It was

expected that the effect of charge-transfer would most strongly manifest itself in the increased bond lengths in the vicinity of N1 and N2 since charge-transfer is expected to terminate on the π^* orbitals of the aromatic ring. What is found is that the C1-N1, C5-N1 and C6-N2, C10-N2, (including all the C-C distances around the rings) are all very close to 1.35 Å for both 2 and 2' and also for 4.

The only remarkable difference for the ion-pairs in the table exists in the bond lengths for both C16-Re and C17-Re. As can be seen from the table, the difference between the ion pairs, 2 and 2' and 4 is approximately ≥ 0.1 Å. Since both 2 and 2' display this difference versus 4, it can not be due to any effect arising to charge-transfer. It most likely is the natural bond length displayed by the cation despite the presence of an electron donor such as tetracarbonylcobaltate ion. The explanation for the lack of any remarkable differences in the bond lengths for the cation can most likely be attributed to a weak interaction between the anion and the cation.

The only faintly remarkable physical differences between 2 and 2' (other than the different structures) which distinguishes them are the bond angles associated with the anion. From the table, the distortion in the anion is more pronounced for ion-pair 2 versus 2'. The average C-Co-C bond angle for both 2 and 2' is 109.4°; however, the standard deviation for 2' is smaller by 0.4° versus 2 (2.1° for 2' vs. 2.5° for 2).

IR spectra supported the existence of an associated contact ion-pair in both the solid and solution phases. IR spectra were obtained in THF and solid KBr pellets (0.1 - 0.5 % mass/mass of complex to KBr). It is known that a close ion pair interaction in an ion-pair with tetracarbonylcobaltate as the anion would tend to distort the carbonyl stretching frequencies of the anion [62]. Normally, an anion in a perfectly symmetrical environment has one stretching frequency at 1892 cm^{-1} for the carbonyls as shown by experimental confirmation. More than one stretching frequency for the carbonyl stretches would serve to indicate that the symmetrical environment of the tetrahedral carbonyls was perturbed by electronic interaction [63].

Table 2.15 illustrates the carbonyl stretching frequencies observed for Co(CO)_4^- in various ion-pairs including those of 2 and 3. In the ion pairs with cations such as NCP^+ , and Na^+ , the stretching frequencies observed in the carbonyl region are clearly due to the anion; however, for 2 and 3, the cation also contributes IR peaks to the carbonyl region which obscure the carbonyl stretches from the anion. Upon closer inspection of Figure 2.19 and 2.20, both the IR spectra for 2 and 3 show two additional, albeit weak, carbonyl peaks near the strong carbonyl peak for the cations. These weak carbonyl peaks must be due to the anion since the cation does not show these peaks in its spectrum. Therefore, based on the IR of a analogous ion-pair such as $[\text{NCP}^+, \text{Co(CO)}_4^-]$, these additional peaks support the hypothesis of a similar interaction in 2 and 3 (similar in structure

to $[\text{NCP}^+, \text{Co}(\text{CO})_4^-]$, see Figure 2.2). In fact, an IR spectrum of the ion-pair $[\text{NCP}^+, \text{Co}(\text{CO})_4^-]$ in THF shows that in addition to a band at 1878 cm^{-1} , it has three other bands at 2006, 1911, and 1870 cm^{-1} . These bands do not differ much in going from the solid to the solution phase (THF has a low dielectric constant) indicating that the strength of the interaction appears to remain fairly constant.

Moreover, x-ray work on $[\text{NCP}^+, \text{Co}(\text{CO})_4^-]$ verifies that the geometry is not in fact tetrahedral (T_d) but C_s (one plane of reflection). The IR spectra also provided supporting information about the symmetry of the anion for **2** and **3** since the IR data for them could be directly compared to the data for $[\text{NCP}^+, \text{Co}(\text{CO})_4^-]$. From comparison of x-ray and IR data between **2** and **3** and $[\text{NCP}^+, \text{Co}(\text{CO})_4^-]$, it appears that the anion of **2** and **3** also display C_s symmetry.

Emission studies done in a variety of solvents also help to establish the assertion of a charge-transfer interaction. A strongly polar solvent limits the electronic interaction between the ions of the ion-pairs because in a polar solvent, the ion-pairs exist predominantly as free ions. No charge-transfer can occur in acetonitrile and this assertion was confirmed by the observation that in this solvent the steady-state emission of **2** and **3** paralleled that of **2a** and **3a**.

The steady-state emission is occurring from deactivation of the MLCT excited state (accessed by an excitation wavelength of 355 nm) of the cation for the ion-pairs. Emission quenching occurs as a result of electron transfer from the tetracarbonylcobaltate ion to the luminescent excited state of the cation. Forward

electron transfer from the anion of the ion-pairs is a fairly exothermic process as evidenced by the ΔG_{FET} for the process (Table 2.3). In general, forward electron transfer is exothermic by almost 1.0 eV.

In acetonitrile, emission data for **2** and **3** at concentrations of 2.5×10^{-3} M and 1.2×10^{-3} M, respectively, strongly resemble the emission for **2a** and **3a**. This phenomenon indicates that the ion-pairs are to a large extent separated as free ions. The separated ions for the ion-pairs are thus not able to engage in electron transfer very efficiently and therefore the emission spectra would be a reflection of emission from the non-quenched excited state cation (the emission spectra should be equivalent to the emission for **2a** and **3a**).

In the free ion state, electron transfer from $\text{Co}(\text{CO})_4^-$ to Re can only occur via dynamic diffusional quenching. If a classic Stern-Volmer quenching paradigm is invoked, at a concentration of 1.0×10^{-4} of **1** in CH_3CN (assuming that the ion-pair is completely separated) the efficiency of quenching is only about 20 % (τ^0 of the cation = 224 ns and $k_q = 3.6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, Table 2.10). Notice that the emission spectra in acetonitrile for **2** and **3** (at concentrations near 0.1 mM) are nearly identical in intensity with those of **2a** and **3a** (see Figures 2.13 and 2.14). These experimental results confirm that the electronic interaction between the anion and the cation for the charge-transfer ion-pairs has been greatly diminished by acetonitrile, a very polar solvent that strongly solvates the ions and thus separates them in solution.

However, in solvents such as THF in which ion-pairing is much more strongly favored, the emission spectra of 2 and 3 becomes greatly attenuated versus that of 2a and 3a (see Figures 2.13 and 2.14). The contact ion-pair is much more favored in non-polar solvents such as THF. Since the ion-pair is intimately associated, static quenching of the excited MLCT state of the cation occurs. As a result of the static quenching, the emission spectra for 2 and 3 versus 2a and 3a were strongly attenuated at concentrations which were similar to those used for the emission studies in CH_3CN .

If the charge-transfer band of a solution of 2 that is mostly ion-paired in THF (1.0×10^{-3} M, 85 % ion-pairs as from Figure 2.10) is directly irradiated using 532 nm light, no luminescence is obtained. The charge-transfer excited state of 2 is not emissive.

Intensity and Energy of the Charge-Transfer Interaction

As described earlier, the intensity of the charge-transfer interaction was determined by the method of Drago and Rose. Figure 2.6 lists the equilibrium constants for the equilibrium of all the ion-pairs as described in Scheme 2-2 and Table 2.5 lists the reduction potentials of the cations. As shown in the table, a definite pattern emerges: the energy of the charge-transfer band ($h\nu_{\text{CT}}$) is dependent on the reduction potential of the cation.

First of all, the reduction potentials become more negative in going from 1 to 3 (i.e., the electron affinities decrease). The reduction potentials are determined largely by the LUMO energy. The LUMO is the π^* , π^* level of the diimine ligand which increases in energy as the ligand is substituted with electron-donating substituents. The energy of the LUMO is thus lowest for 1 which has two electron-withdrawing ester groups ($E_{1/2} = -0.63$ eV) and it is highest for 3 which has four electron-donating methyl groups ($E_{1/2} = -1.42$ eV).

From Mulliken Theory, charge-transfer energy is known to be a function of the ionization energy of the donor and the electron affinity of the acceptor. Since the ionization energy is constant throughout the series of ion-pairs (tetracarbonylcobaltate ion is the donor in each case), only the electron affinity or the reduction potential of the cation needs to be considered for the correlation of the charge-transfer energy among the ion-pairs. Figure 2.12 shows the dependence of the charge-transfer energy on the reduction potential of the cation. The charge-transfer energy increases as the reduction potential of the cation becomes more negative. The Mulliken relationship holds in this series of ion-pairs. In fact, the agreement between the energy of the charge-transfer band maximum and the reduction potential is quite good ($R^2 = 0.99$) in the series partly because the structural differences among the cations are minimal and as a result the work terms in the Mulliken Relationship are fairly constant (see eq. 2-17). Also evident in Table 2.3 is a decrease in the charge-transfer intensity as the energy of the charge-

transfer increases. Although the latter result is not necessarily always true for ion-pair interactions, it is always true that the decrease in $E_{1/2}(A/A)$ is mirrored by a decrease in $h\nu_{CT}$.

Figure 2.12 highlights this relationship for both the charge-transfer ion-pairs of this study and those shown in Table 2.2. Notice the strong similarity between the two sets of data. The similarity observed in the Mulliken plot between the charge-transfer ion-pairs of this study and those of Table 2.2 is in part a result of the structural similarities between the pyridinium ion-pairs and the Re ion-pairs.

In Figures 2.4 and 2.17 which show the x-ray structures for $[PP^+, Co(CO)_4]$ and **2**, respectively, it can be seen that the charge-transfer interaction occurs between the tetracarbonylcobaltate ion and an aromatic nitrogen heterocycle. Thus, the Mulliken Relationship in Figure 2.13 is similar for the two different ion-pairs because (1) the reduction potentials for the cations of each set (pyridinium and Re) are a function of the π^* LUMO's of the nitrogen heterocycles and (2) the similarity of the x-ray structures.

The intensity of the charge-transfer interaction is dependent upon the degree of electronic coupling between the anion and the cation. For all the ion-pairs in Table 2.2 and Table 2.5, the extinction coefficients are very low (less than $600 \text{ M}^{-1}\text{cm}^{-1}$) indicating that the electronic overlap between the electron donor and acceptor is poor. In fact, IR and x-ray data also show that the charge-transfer

interaction is not very strong for **2**. IR is a very sensitive probe to the environment in which a molecular species resides. The shape, energy, and multiplicities of the stretching frequencies exhibited by a particular set of atoms in a molecule are influenced by different solvents or intermolecular interactions.

Solid and liquid phase (THF) IR spectra of **2** were obtained and showed a very strong similarity. Three sets of bands were observed in the solid phase which were very similar in shape and energy to those in the solution phase (See Figure 2.19 and 2.20 and Table 2.15 for values). This result suggests that the geometry exhibited in the solid phase is also present in the solution phase. This hypothesis is supported by referring to the ion-pairs in Table 2.2. In these ion-pairs, the difference in charge-transfer energy between the solution and solid phases may be accounted for by solvation. In the solution phase, the charge-transfer energy is principally decreased due to the ion solvation. Figure 2.27 shows the solid (10% silica) and solution phase (CH_2Cl_2) electronic spectra of $[\text{Q}^+, \text{Co}(\text{CO})_4^-]$. Notice the strong resemblance in terms of shape and absorption maximum.

The choice of solvent has a very pronounced effect on the energy of charge-transfer. It was found for instance that in acetonitrile the charge-transfer band for **2** almost completely disappeared. The absorption spectra for solutions of **2** in benzene, THF, and acetonitrile are shown in Figure 2.8. As can be observed in Figure 2.8, the charge-transfer band of **2** blue-shifts as the polarity of the solvent increases. In fact, the shift is quite pronounced in going from a well-defined

charge-transfer band with a maximum at 564 nm in benzene to a less defined charge-transfer band whose maximum can be approximated by inspection to be 500 nm, to a weak shoulder in acetonitrile whose maximum is deep within the intraligand absorptions. A strongly polar solvent is known to raise the energy of charge-transfer as a result of increasing the outer-sphere reorganization energy. In brief, the outer sphere reorganizational energy is the energy required to reorient the solvent dipoles in order to accommodate the electron transfer event (which of course disturbs the existing solvent dipole shell around the reactants). Because an increase in the reorganizational energy will tend to disfavor an electron transfer process, the energy for the event in **2** consequently increases (hence, the blue-shifting of the charge-transfer band). Likewise, a non-polar solvent decreases the charge-transfer energy by decreasing the reorganization energy.

From an x-ray structure of **2**, it is postulated that charge-transfer occurs via an interaction mediated by the remote carbonyl oxygens, O4 and O5 of the tetracarbonylcobaltate ion to the nitrogens, N1 and N2 of the diimine of the cation. The average distance between the carbonyl oxygens and the diimine nitrogens is 3.3 Å. The charge-transfer is characterized as an outer-sphere MLCT (OS-MLCT), one of very few cases reported in the literature [64]. The p orbitals of the oxygen are presumed to bridge the transport of the charge between the cobalt and the π^* , π^* levels of the diimine. Since the overlap is not expected to be particularly strong, the charge-transfer interaction is not particularly strong as

evidenced by the weak extinction coefficients measured in THF solution for charge-transfer.

Evaluation of the Static and Dynamic Quenching of the MLCT Excited State of the Cation

Since there is no emission from the ion-pair, any emission must occur from free cations. To confirm this hypothesis, a Stern-Volmer plot was made of the lifetime data in for **2** in THF and the data did indeed obey a linear relationship with a value for dynamic quenching of $7 \times 10^{10} \text{ s}^{-1}$ (Figure 2.15). This value is large for diffusion controlled kinetics and suggests that other quenching mechanisms may be operating in addition to dynamic quenching. Another possible quenching mechanism is aggregation of the ion-pairs.

Debye-Huckel calculations were done to determine the theoretical limit for dynamic quenching of ion-pairs whose interatomic distance for charge-transfer is known [54].

It has already been discussed that charge-transfer absorption can only occur for ion-pairs associated in the ground state. **1**, **2**, and **3** can not only engage in optically-induced charge-transfer within the ion-pair, but can also engage in MLCT-sensitized static or dynamic (diffusional quenching) charge-transfer.

In general for **1**, **2**, and **3**, the MLCT excited state of a free cation in solution may be quenched by intermolecular diffusional electron transfer from the

electron donor (tetracarbonylcobaltate) to the excited cation. The intermolecular diffusional electron transfer quenching process is characterized by a second order rate constant, k_q . If the excited cation and the anion are in intimate contact as part of an ion-pair, then static quenching of the excited state of the cation by the anion is the primary quenching pathway available to the ion-pair.

It was believed that the lifetime of the ion-pair at an excitation of 355 nm would be a reflection of the deactivation of the MLCT state of the cation.^b At concentrations in which there existed 75% or greater ion-pairing (1.0×10^{-3} in THF), the single-exponential lifetimes of **2** in THF varied over a fairly large range. Double exponential fits of the emission decays did not distinguish a static from a dynamic quenching component. This confirmed the earlier observation afforded by steady-state emission experiments that no emission could occur from the ion-pair. All emission was therefore occurring from free excited cations that were quenched by typical intermolecular diffusional quenching. The quenching rate constant obtained from a Stern-Volmer treatment of the time-resolved emission of **2** in THF was $7 \times 10^{10} \text{ s}^{-1}$ which is larger than the diffusional limit maximum calculated k_q of $4 \times 10^{10} \text{ M}^{-1} \text{ cm}^{-1}$ from Debye-Huckel calculations. Since the experimental value is larger than the diffusional limit, it is possible that other mechanisms beside dynamic quenching were in effect and it was decided to

^b No emission occurs after excitation of the ion-pairs at 532 nm as evidenced by the steady-state emission experiments

uncover any hidden quenching components by steady-state luminescence experiments.

Steady-state experiments involved obtaining the luminescence of a solution of **2a** in THF and comparing it to **2** (both absorbances were matched at 355 nm). All data for **2** is shown in Table 2.5. From this data a quenching constant of $4 \times 10^{11} \text{ s}^{-1}$ was obtained which supported the existence of hidden quenching components. This value is six times larger than what was calculated from the lifetime experiments.

Figure 2.28 illustrates three means of quenching available to the ion-pair. Mechanism A represents static quenching which defines the quenching available in an ion-pair. Mechanism B shows typical diffusional quenching which is characterized by a second order Stern-Volmer constant. Mechanism C, however, is a mixture of the other two mechanisms since it includes them in an aggregation quenching mechanism. According to Mechanism C, a free excited cation may by associating to an ion-pair via dipole-dipole interaction be quenched by the anion of the ion-pair. The opportunity for aggregation should increase as the concentration of the ion-pair increases, enhancing the rate of quenching. The theory for aggregation of the ion-pairs leading to electron transfer quenching of the excited cation receives some support from x-ray data. An x-ray of **2** showed two distinct ion-pairs, one of which may not support charge-transfer. Since the solution state spectroscopic data for the ion-pairs has been shown to bear some parallels to the

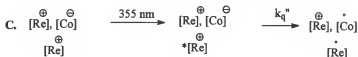
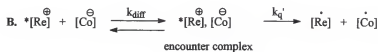


Figure 2.28. Quenching mechanisms (A, B, and C) that are available to the ion-pairs in which the cation is represented as $[\text{Re}^{\oplus}]$ and the anion as $[\text{Co}^{\ominus}]$: **A:** Static quenching, characterized by rate constant, k_q ; **B:** Dynamic quenching, characterized by rate constant, k_q' ; and **C:** An aggregation type complex whose quenching is a mixture of mechanism A and B, and is characterized by a rate constant, k_q'' .

data from the solid state, it is suggested that THF may support aggregation of the ion-pairs leading to ET quenching of the excited cations.

Lifetime experiments for **2** in benzene, however, does not follow a Stern-Volmer relationship (See Table 2.9). This behavior may arise because benzene is much more non-polar than THF and the ion-pair equilibrium therefore strongly favors the ion-pair. Since there are mostly ion-pairs, a very small concentration of free cations are present in solution that can emit upon excitation. It is suggested that the concentration of free cations is constant since the lifetimes do not change significantly for a broad concentration range (See Table 2.7).

Cage Escape Yields as a Function of Excitation Wavelength

One of the objectives of this work was to evaluate the difference in cage escape yields for the ion-pairs after MLCT (355 nm) and charge-transfer (532 nm) excitation. Figure 2.6 clarifies the pathways which can be accessed by the two distinct excitation wavelengths. The cations of the ion pairs have their own excited states, the MLCT excited states, which are fairly good oxidants (See Table 2.3). Electron transfer quenching of the MLCT state by tetracarbonylcobaltate is a very exothermic process as demonstrated by the ΔG_{FET} 's in the table).

Also note that in addition to MLCT-sensitized charge-transfer, the ion-pair has available an optical charge-transfer absorption which directly leads to redox

products. According to Figure 2.6, both excitation wavelengths lead to a geminate ion-pair which can separate in solution.

Transient absorption spectra of **2** were obtained in THF at both 355 nm and 532 nm excitation. As illustrated in Figure 2.23, compared to the actual reduced cation of **2a** shown on top, the spectrum obtained with 355 nm excitation (middle) at a concentration of $2 = 1.0 \times 10^{-4}$ M in THF distinctly shows the reduced cation moiety with the signature absorption peaks at 350 and 490 nm. The bottom spectrum obtained with 532 nm excitation ($[2] = 1.0 \times 10^{-3}$ M) showed the same absorption pattern representative of the reduced cation except that the absorption intensity was weaker. This was the first qualitative clue that a difference existed in the yield of free reduced cation between the two modes of excitation.

It was found that the yield of free reduced cation was much greater for 355 nm as opposed to 532 nm excitation (results are shown in Table 2.17). Irradiation of the cation with 355 nm excitation light produces a triplet excited state. When the excited cation and anion are in the geminate ion pair, the excited state of the cation can be quenched by the anion to generate a triplet radical-pair. It is known from spin mechanics that a triplet radical pair has a much longer lifetime than the analogous singlet radical pair [2]. A triplet state has a much lower probability of recombination for decay since the electron spins are not paired. The triplet state must undergo intersystem crossing to the singlet state which can decay to the ground state. After the MLCT excited state of the cation is quenched by electron

transfer from the anion, a triplet radical-pair is generated. The triplet radical-pair cannot directly decay to the ground state and thus has a larger window of opportunity than the singlet radical-pair to escape the cage in which it was born.

532 nm excitation of the charge-transfer ion-pair generates a geminate radical ion-pair that is singlet in character. As stated above, a singlet state can recombine much more rapidly than a triplet state since the spins are already paired. The quantum yields for cage escape shown in Table 2.17 therefore demonstrate a lower yield of reduced cation for 532 nm excitation as opposed to 355 nm excitation.

Support for the singlet character of the excited charge-transfer ion-pairs, **2** and **3** was obtained from transient absorption experiments with $[Q^+, Co(CO)_4]$ (See Figure 2.2 for structure). The quantum yield of free reduced Q^+ arising from both the 532 nm and 355 nm excitation was studied. It is known from the literature that the singlet state of the cation and the ion-pair may be accessed by 355 nm and 532 nm excitation, respectively. It was found at both excitation wavelengths that the yields of reduced cation were low ($< 4\%$, see Table 2.17). This result lent support to the hypothesis of the singlet character of the excited states of the charge-transfer ion-pairs (**2** and **3**) obtained with 532 nm excitation.

Conclusions

Several important facts have emerged from the ion-pair studies. The ion-pairs possess a unique charge-transfer absorbance band not evident in the spectra of the starting materials. Excitation into this charge-transfer band with 532 nm light produces a geminate radical ion-pair. The radical ion-pair is believed to possess singlet character and therefore cannot undergo efficient cage escape from the geminate radical ion-pair since the rate of decay for the singlet state is much faster than the rate of cage escape. The latter result is corroborated from analogous cage escape transient absorption work done with $[Q^+, Co(CO)_4]$.

MLCT excitation (355 nm) of the cation populates an excited state of triplet character. This state can sensitize electron transfer from the anion to generate a triplet ion-pair. Since direct return to the ground state from the triplet state is prohibited, the triplet must undergo intersystem crossing to the singlet state; thus, the triplet state possesses a longer lifetime than the singlet state. As a result of this longer lifetime, the excited triplet state accessed by 355 nm has a greater opportunity than the excited singlet state to undergo cage escape. The latter result is supported by transient absorption experiments which show that cage escape yields for 2 and 3 are fifteen times greater at 355 nm versus 532 nm excitation (See Table 2.17 for yields).

Steady-state emission experiments show that no emission occurs from the charge-transfer excited state at 532 nm excitation. MLCT emission is observed from THF solutions of **2** and **3** that are excited at 355 nm. Time-resolved emission studies have demonstrated that the Stern-Volmer rate constant for quenching of the MLCT state is $7 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ in THF. A similar Stern-Volmer treatment of the steady-state emission demonstrates a rate constant for quenching of $4 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$. Clearly, there is a "hidden" component of quenching in addition to dynamic quenching of the MLCT state of the cation. The hidden component is due to static quenching within the ion-pairs. In essence, no emission is observed from the ion-pairs because $\text{Co} \rightarrow \text{Re}$ electron transfer is so rapid. The excited cations are quenched by the anion of the ion-pair to which they have associated.

An x-ray structure of **2** lends qualitative support to the concept of aggregation in the ion-pairs. X-ray structures illustrate two distinct ion-pairs in the unit cell, one of which is believed to be active in charge-transfer. It is entirely plausible, therefore, that the ion-pairs may engage in more than 1:1 interactions between the members at increasing concentrations.

An x-ray structure of **2** demonstrates two ion-pairs in the unit cell, one of which is believed to engage in charge-transfer. From the x-ray structures, the ion-pair which is believed to be active in charge-transfer shows two carbonyl oxygens of the anion that are directly pointed to the diimine nitrogens of the cation. Since no significant evidence for this charge-transfer interaction was provided by the

bond length and angle data, it is therefore suggested that the orbital interaction is weak. The hypothesis of a weak interaction between the anion and the cation in the solid state is supported by IR and electronic absorption spectra of **2** and **3**. Since IR data lend support to the belief of a similar ion-pair geometry in both the solid and solution phases, it can be concluded from the weak extinction coefficient for charge-transfer in THF (for both **2** and **3**) that the interaction between the anion and the cation in the solid is also fairly weak.

Finally, it is worth noting that the cage escape yields for **2** and **3** after MLCT excitation do not appear to depend much, if at all, on ΔG_{BET} . The cage escape yield for the cation of **3** is only 2% higher than for **2**. It was expected that the difference would have been larger since the ΔG_{BET} (see Table 2.3 for values) for **2** and **3** vary by 220 mV. Since the ΔG_{BET} values fall in the Marcus inverted region, it is expected that the rate of back electron transfer should decrease as its exothermicity increases. Previous calculations have shown the efficiency for cage escape of the cation of **2** with DABCO as the electron donor is 10% larger than for **3** [51]. Since the errors on all the cage escape yield calculations are $\pm 5\%$, it is safe to conclude that the cage escape yield difference between **2** and **3** falls within experimental error.

Experimental

Reagent grade solvents and chemicals were used for synthesis without purification unless otherwise noted. Chromatography was done by using either Merck silica gel 60 (230-400 mesh) or neutral Alumina (Brockman Grade III) from Fisher.

Re(CO)₅Cl. CCl₄ was dried over 4 Å molecular sieves and 10.0 g (15.8 mmol, Strem) of Re₂(CO)₁₀ was dissolved into 275 mL of CCl₄ which was transferred to a pyrex test tube. The solution was stirred, capped with a rubber septum and sparged with CO gas (Matheson) for 10 minutes. The pyrex vessel was irradiated by a 450 W medium-pressure mercury Hanovia lamp which was placed 10 cm away from the stirring solution. The reaction was monitored by IR which indicated the disappearance of the starting material bands at 2070, 2013, and 1973 cm⁻¹. After one hour, > 95 % of the starting material had been photolyzed and a thick, off-white precipitate was observed in the test tube. The precipitate was collected by filtration and the supernatant solution was placed back in the tube, resparged with CO, and irradiated for an additional hour. The filtration and irradiation procedures were repeated. The crude product was purified by recrystallization in 2/1 v/v methanol/acetone (200 mL total volume) with cooling to -15^o C overnight. The recrystallized Re(CO)₅Cl was obtained as white crystals, yield 9.3 g (75%).

(b)Re(CO)₃Cl. (b) = 2,2'-bipyridine (abbreviated as *bpy*); 2, 2'-(4, 4'-5, 5'-tetramethyl) bipyridine (abbreviated as *tmb*); 5,5'-(N, N, N', N'-tetraethylamido)bipyridine (abbreviated as *deab*).^a (See **Metathesis of (b)Re(CO)₃Pyr, PF₆⁻ → (b)Re(CO)₃Pyr, Cl** for conversion of *deab* complex to *dmeb* complex where *dmeb* = 5, 5'-dimethoxycarboxyl.) The synthesis of the *bpy*, *tmb*, and *deab* complexes was done as illustrated by the following synthesis for (bpy)Re(CO)₃Cl: into 15 mL of ACS grade toluene, 400 mg (1.11 mmol) of freshly recrystallized Re(CO)₃Cl was suspended and 185 mg (1.19 mmol, 1.1 equivalent) of *bpy* ligand (Aldrich, > 98 % purity) was added to the suspension. The suspension was allowed to stir under a nitrogen atmosphere while it refluxed for one hour. After this period, the product was apparent as a yellow precipitate. After 1 hour of reflux, the suspension was allowed to cool and the yellow product was collected by suction filtration on a 15 mL medium-porosity fritted funnel. The product was washed with 3 x 10 mL portions of toluene to remove the excess unreacted bipyridine ligand. After drying the solid in vacuo for several hours to remove the toluene, the product was obtained as a bright yellow solid, yield 492 mg (96 %).

^a Note that the ion-pair based on the cation of **1** (see Figure 2.6 for structure) was synthesized only after the (deab)Re(CO)₃Cl complex was hydrolyzed in methanol to the diester. See **Metathesis of (b)Re(CO)₃Pyr, PF₆⁻ → (b)Re(CO)₃Pyr, Cl** section.

(bpy)Re(CO)₃OSO₂CF₃. (bpy)Re(CO)₃Cl (300 mg, 0.65 mmol) was suspended in 5 mL of methylene chloride that had been freshly distilled over CaH₂. The suspension was stirred under nitrogen while 0.6 mL (15 equivalents) of trifluoromethanesulfonic acid^b ("triflic acid") was slowly added dropwise to the suspension over 30 seconds. The suspension immediately became a transparent yellow solution which was allowed to stir for 1 hour. The reaction was monitored by silica gel TLC (9/1 CH₂Cl₂/CH₃CN) which showed that the very bright, (under long-wave UV illumination, i.e., 365 nm light) higher R_f starting material (R_f = 0.7) disappears immediately and is replaced by a pale yellow material at R_f = 0.3. The reaction was quenched by addition of 50 mL of dry diethyl ether and after about 1 minute of stirring the solution became cloudy with a light yellow precipitate. The precipitate was collected on a 15 mL medium-porosity fritted funnel and washed with copious amounts of diethyl ether to remove excess triflic acid. The product was dried in vacuo for several minutes to remove any ether and was obtained as a bright yellow solid, yield 325 mg (87 %).

^b Trifluoromethanesulfonic acid ("triflic acid") is an extremely strong acid that should be handled with care and only in a well-ventilated hood. It was refrigerated and stored under argon in a Schlenk tube after the ampoule was opened.

(bpy)Re(CO)₃Pyr, PF₆⁻ 200 mg (0.35 mmol) of freshly prepared (bpy)Re(CO)₃OSO₂CF₃ solid was dissolved in 10 mL of freshly distilled THF that had been dried over Na/K. To this cloudy solution under nitrogen, 60 μ L of pyridine (Fisher) was added by syringe. While the solution was stirring at room temperature, 593 mg of ammonium hexafluorophosphate (3.9 mmol, Aldrich) was added at which point the solution became clear yellow. The reaction was monitored by silica gel TLC with 9/1 CH₂Cl₂/CH₃CN as the eluent. At time (T) = 0, the starting material was apparent at R_f = 0.3 and a darker yellow spot at R_f = 0.6 could also be seen. Over the course of 30 minutes, the R_f = 0.6 spot gradually diminished to give rise to a darker yellow spot at R_f = 0.7.

After 2 hours, the reaction was discontinued and the solvent was removed under reduced pressure. The yellow solid was dissolved in 9/1 CH₂Cl₂/CH₃CN, placed on a chromatography column packed with Merck Kieselgel (10 cm x 2 cm), and eluted with the same solvent. The fractions were combined, the solvent removed under reduced pressure, and the solid dried overnight. The product was obtained as a bright yellow solid, yield 165 mg (94 %).

Na⁺, Co(CO)₄ [62]. Sodium hydroxide pellets (10 g, 435 mmol, Fisher) were powdered in a drybox by using a mortar and pestle and dried overnight in a

^a (tmb)Re(CO)₃Pyr, PF₆⁻ and (deab)Re(CO)₃Pyr, PF₆⁻ were synthesized by a procedure already published in the literature: see D. Brent MacQueen and Kirk S. Schanze. *J. Am. Chem. Soc.* **1991**, *113*, 7470

drying pistol under ethanol reflux and 0.250 mTorr pressure. The drying pistol was brought into a nitrogen atmosphere drybox and the powdered sodium hydroxide was transferred to a Schlenk tube. Into the Schlenk tube, 1.66 g of chilled $\text{Co}_2(\text{CO})_{10}$ (4.17 mmol) was added quickly since it has a very low vapor pressure at room temperature and is quite toxic. A large stirbar and 35 mL of dry THF (Na/K, benzophenone) were added to the solids which did not dissolve in the THF. The Schlenk tube was sealed with a greased glass stopcock and taken out of the drybox. The THF suspension was kept under argon and allowed to stir for several hours.

The reaction was discontinued after 3 hours had elapsed and the solution was transferred to another Schlenk tube via a filter cannula. The solution which was pale yellow was evaporated under reduced pressure overnight. A bright white solid was observed in the Schlenk tube which was weighed in the drybox for a yield of 0.5 g (62 %).

Metathesis of (b)Re(CO)₃Pyr, PF₆⁻ → (b)Re(CO)₃Pyr, Cl⁻. To 20 mL of methanol and 5 mL of acetonitrile, 85 mg of [(bpy)Re(CO)₃Pyr, PF₆⁻] (1.3 mmol) was added and dissolved by sonication over one hour. Meanwhile, 7 g of Dowex chloride anion exchange resin # 1 x 2-100 (Aldrich) was suspended in methanol and allowed to soak for one hour. A 10 cm x 1.5 cm chromatography column was packed with the pre-soaked Dowex resin and charged with excess chloride by

eluting with a 50 mL methanol solution of 0.05 M tetrabutylammonium chloride (TBACl). Excess TBACl was rinsed off the column by eluting with excess methanol (75 mL). The methanol/acetonitrile solution of $[(bpy)Re(CO)_3Pyr, PF_6^-]$ was passed through the column using methanol as the eluant. The methanol/acetonitrile solvent was removed under reduced pressure leaving a shiny, bright yellow solid, yield 73 mg (95 %). $[(deab)Re(CO)_3Pyr, PF_6^-]$ was converted to the diester complex $[(dmeb)Re(CO)_3Pyr, PF_6^-]$ upon methanol elution through the Dowex column.

2. The synthetic procedure described below applies to **2**, but it also was followed for the synthesis of **1** and **3** (see Figure 2.6 for acronyms). 35 mg of freshly prepared $Na^+, Co(CO)_4^-$ (0.18 mmol, 1.3 equivalents) was weighed into a Schlenk tube in the drybox. During this time, 100 mL of triply distilled water was degassed for several hours by a fritted nitrogen bubbler. Then 4 mL of the water was transferred by cannula to the $[Na^+, Co(CO)_4^-]$ which dissolved instantly. The aqueous $[Na^+, Co(CO)_4^-]$ solution was maintained under a blanket of argon while 85 mg of freshly prepared $[(bpy)Re(CO)_3Pyr^+, Cl^-]$ was placed in a Schlenk tube and then dissolved by addition of 14 mL distilled water, 5 mL of methanol, and 1 mL of acetonitrile. The $[(bpy)Re(CO)_3Pyr^+, Cl^-]$ solution was degassed well. At this point the room lights were turned off and the Schlenk tube containing the $[(bpy)Re(CO)_3Pyr^+, Cl^-]$ solution was covered with aluminum foil. The aqueous

$[\text{Na}^+, \text{Co}(\text{CO})_4^-]$ solution was then slowly added via cannula to the $[(\text{bpy})\text{Re}(\text{CO})_3\text{Pyr}^+, \text{Cl}^-]$ solution. **2** was instantly visible as a dark red precipitate. The mixture was allowed to stir for one hour. The solvents were then removed under reduced pressure overnight. A dark-red product was observed in the bottom of the flask which was washed twice with distilled water to remove any soluble salts (e.g., NaCl). The product was obtained as a dark-red solid, yield 90 mg (100 %).

2 was recrystallized by first dissolving 90 mg in less than 1 mL of degassed acetonitrile and then allowing this layer to settle. More acetonitrile was added by trickling it down the sides of the Schlenk tube drop-wise (0.2 mL), and covering these layers with 2 mL of dry, degassed diethyl ether (from Na/K still). This system was kept under a positive pressure of argon and stored in a dark, cool corner of the lab. After 2 days, most of the solvents had evaporated leaving long, sharp, dark needles of crystals from which an x-ray structure of **2** was obtained. Unfortunately, **1** and **3** did not recrystallize.

Quinolinium cobaltate [46]. To a 200 mL round bottom flask, 1.5 mL of quinoline and 5 mL (excess) of methyl iodide were added while stirring. An orange-colored precipitate was observed as the reaction stirred overnight. The orange product was washed with toluene and hexane and allowed to dry. The orange product was metathesized to the PF_6^- salt by dissolving it into water and

adding excess ammonium hexafluorophosphate until a white precipitate was formed. The white product, quinolinium PF_6^- was then metathesized to the chloride, quinolinium chloride by dissolving it in methanol and eluting it through a chloride exchange chromatography column.

Sodium tetracarbonylcobaltate (400 mg, 2.1 mmol) was dissolved in distilled water and allowed to stir while 610 mg (3.7 mmol) of quinolinium chloride was simultaneously dissolved in 1 mL of water. Quinolinium chloride was transferred to the sodium tetracarbonylcobaltate solution via cannula and a dark red precipitate could be observed forming in the water during the transfer. The aqueous mixture was allowed to stir for three hours after which the solvent was filtered off, the product was washed twice with water, and allowed to dry under reduced pressure. The product was collected in the dry box, yield 0.51 g (81 %). All spectroscopic characterization has been previously published [46].

1 Spectral and Analytical Data: ^1H NMR (300 MHz, CD_3CN) δ 4.10 (s, 6H, methyl), 7.27 (t, 2H, pyridine), 7.85 (t, 1H, pyridine), 8.20 (d, 2H, pyridine), 8.53 (d, 2H, dmeb), 8.73 (d, 2H, dmeb), 9.63 (s, 1H, dmeb). Anal. Calcd. for $\text{C}_{26}\text{H}_{17}\text{N}_3\text{O}_{11}\text{Re}_1\text{Co}_1$: C, 39.35; H, 2.16; N, 5.30; Found: C, 32.15; H, 2.42; N, 5.10. Low-resolution positive MS (FAB) calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_7\text{Re}$, 621.6, found, 622 (Mass of cation). Cyclic voltammetry data. CH_3CN . 0.1 M

tetrabutylammonium hexafluorophosphate as supporting electrolyte; vs. SCE: $E_{1/2}(\text{Re}^{\text{II}}/\text{Re}^{\text{I}}) = -0.63 \text{ V}$, $E_{1/2}(\text{Co}^{\text{II}}/\text{Co}^{\text{I}}) = +0.20 \text{ V}$ (irreversible).

2 Analytical Data: ^1H NMR (300 MHz, CD_3CN) δ 7.29 (t, 2H, pyridine), 7.79 (t, 1H, pyridine), 8.06 (t, 2H, pyridine), 8.26 (t, 2H, bpy), 8.39 (d, 2H, bpy), 8.60 (t, 2H, bpy), 9.21 (d, 2H, bpy). Anal. Calcd. for $\text{C}_{22}\text{H}_{13}\text{N}_3\text{O}_7\text{Re}_1\text{Co}_1$: C, 39.06; H, 1.94; N, 6.21; Found: C, 38.81; H, 1.99; N, 6.14. IR (KBr) 2026, 1937, 1923, 1880.

3 Spectral and Analytical Data: ^1H NMR (300 MHz, CD_3CN) δ 2.44 (s, 6H, methyl), 2.46 (s, 6H, methyl), 7.30 (t, 2H, pyridine), 7.86 (t, 1H, pyridine), 8.10 (s, 2H, tmb), 8.28 (d, 2H, pyridine), 8.87 (s, 2H, tmb). Anal. Calcd. for $\text{Re}_1\text{Co}_1\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_7$: C, 42.63; H, 2.89; N, 5.74; Found: C, 42.66; H, 3.02; N, 5.64. IR (KBr) 2032, 1948, 1922, 1877.

Instrumentation/Experimental

Steady-State Fluorescence Experiments. All emission work was performed with solutions which had been prepared in the drybox ($< 10 \text{ ppm O}_2$). Luminescence work was done with the intention to determine the rate constant for static quenching, k_q^{static} and to compare fluorescence intensities of **2** to **2a**.

A sample procedure is given as follows (note that all preps were carried out in an argon-filled drybox): a stock solution was prepared by dissolving 1.0 mg of **2**

in THF within a 25.0 mL volumetric flask. The concentration of the stock solution was 5.8×10^{-5} M and was consecutively diluted as shown in the chart below. The absorbance at 350 nm was taken for each solution on a HP 89532A diode-array spectrophotometer and emission spectra were recorded ($\lambda_{\text{exc}} = 355$ nm and $\lambda_{\text{em}} = 600$ nm).

A stock solution was prepared in THF by dissolving 2.2 mg of **2a** in 25.0 mL for a concentration = 1.5×10^{-4} . This solution was diluted to make 5 solutions whose absorbances matched those of **2** at 350 nm.

Volume of Stock added	Final Volume	Resulting Concentration
1	10	5.8×10^{-6}
2	10	1.2×10^{-5}
3	10	1.7×10^{-5}
4	10	2.3×10^{-5}
1	1	5.8×10^{-5}

The absorbances were checked and luminescence spectra were taken. Stern-Volmer plots were generated by using the following equation: $I^0/I = 1 + k_q\tau^0 [2]$, where I^0 is the emission intensity of the solution of **2a** having a matched

absorbance at each concentration of **2** and **1** is the emission intensity of the solution of **2** and τ^0 is the unquenched lifetime of **2a** (237 ns in THF).

Lifetime Experiments. All lifetime experiments were done on a Photochemical Research Associates (PRA) single photon counting instrument. Solutions were again made up in THF under nitrogen or argon and sealed. The data was fitted with one or two exponentials using the Decan software package [65].

CHAPTER 3
LONG-LIVED PHOTOINDUCED CHARGE SEPARATION PROMOTED BY
RING OPENING OF A PIPERAZINE RADICAL CATION

Introduction

Metal complex dyads, M-D, comprise a transition metal chromophore (M) covalently linked to an organic electron donor (D) [66-70]. Photochemical excitation of these assemblies produces a charge separated state, $M^{\cdot-}D^+$, which has a lifetime that is controlled by the dynamics of the highly exothermic (inverted region) charge recombination reaction [66-67]. In previous studies it has been shown that the lifetime of the charge separated state in M-D assemblies increases with the driving force for charge recombination [66b, 67c] or the separation distance between M and D [67b].

Herein a new approach is reported to increasing the lifetime of a charge separated state in a metal complex dyad which relies on the reversible ring-opening of the radical cation of a piperazine electron donor. Thus, metal complex dyad *c-1* contains the $(bpy)Re^I(CO)_3$ (Re) chromophore ($bpy = 2,2'$ -bipyridine) covalently linked to a 2,3-diaryl-1,4-dimethylpiperazine electron donor. Intramolecular electron transfer from piperazine to the photoexcited Re

chromophore produces a charge separated state in which the Re center is reduced and the piperazine is a cation radical. Carbon-carbon bond fragmentation in the piperazine cation radical produces a new charge separated state in which the donor exists as an open-chain distonic cation radical. The net result is the production of a charge separated state having a lifetime which is 5 to 10-fold longer than observed in structurally related metal complex dyads.

Results

UV-Visible Absorption Spectra

UV-Visible spectra for all complexes were obtained in CH_3CN that was distilled over CaH_2 . All spectra were referenced to CH_3CN blank solutions that were "zero-referenced" at 800 nm. All solutions were prepared under standard room conditions and later argon-degassed for 30 minutes. Solutions of the c-1 complex were prepared in the dark to minimize photodecomposition.

Structures and abbreviations for all complexes are shown in Figure 3.1. Absorbance spectra for c-1 (solid line spectra) and t-1 (dotted line spectra) are shown in Figure 3.2. The absorbance spectra are identical in shape and energy in all regions of the spectrum except from 240 to 300 where the intraligand absorptions for t-1 are about 1.3 times stronger than c-1.

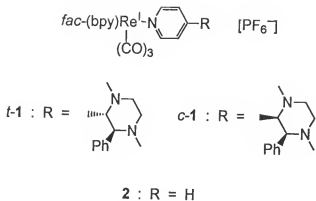


Figure 3.1. Structure and abbreviations for all complexes.

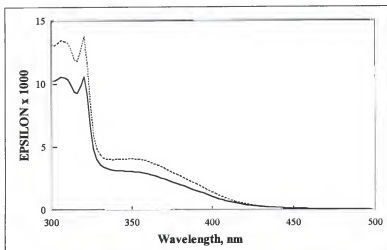


Figure 3.2. Absorbance spectra of c-1 (solid spectra) and t-1 (dotted spectra) obtained in CH_3CN plotted as the extinction coefficient, EPSILON ($\text{M}^{-1}\text{cm}^{-1}$) versus wavelength (nm) at room temperature.

The strong $\pi \rightarrow \pi^*$ intraligand absorptions for c-1 and t-1 extend from 200 to 320 nm, after which they weaken in intensity and the MLCT (metal-to-ligand charge transfer) absorption band gains prominence (from approximately 330 to 420 nm). The MLCT band for both isomers is relatively broad, moderately strong ($\epsilon \approx 4000 \text{ M}^{-1}\text{cm}^{-1}$), and displays a maximum of 350 nm.

^1H NMR Spectra

All ^1H NMR spectra were obtained on either a GE QE-300 MHz or Gemini 300 MHz spectrophotometer. All solutions were made in either CDCl_3 or CD_3CN (0.1% v/v TMS) and kept in the dark to prevent photoisomerization. The ^1H NMR spectra for c-1 and t-1 are displayed in Figure 3.3.

Photoisomerizations were effected by exposing the solution of c-1 [5×10^{-3}] in an NMR tube to a 450 W medium-pressure Hanovia lamp. The NMR tube was maintained at a constant distance of 5 cm for various increments of time and ^1H NMR spectra were obtained after each irradiation and are displayed in Figure 3.4.

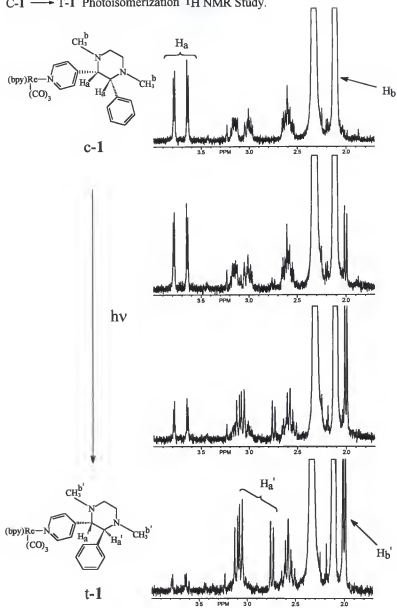
Low-Temperature Emission Spectra

Low-temperature emission spectra were carried out by time-correlated single photon counting on a PRA (Photochemical Research Associates) system. The excitation source was a hydrogen-filled spark gap (PRA, model 570B) preset at a repetition frequency of 3×10^4 Hz. A UG-11 excitation filter was used to



Figure 3.3. The ^1H NMR spectra of *c*-1 (top) and *t*-1 (bottom) obtained in CD_3CN (S) at room temperature.

Figure 3.4. ^1H NMR spectra of the photoisomerization of c-1 to t-1 in CDCl_3 as a function of photolysis time.

C-1 $\longrightarrow$ T-1 Photoisomerization ^1H NMR Study.

select near-UV light and the emission from 595 to 605 was selected by a P10-600 nm emission filter.

2, c-1, and t-1 were prepared in 7/3 butyronitrile/acetonitrile solutions and placed into 3 x 1 cm glass ampoules. The ampoules were attached to a high vacuum line by ground-glass joints that were greased with high-vacuum grease. The solutions were vacuum-degassed by five freeze-pump-thaw cycles (pressures typically attained were 10^{-5} Torr). The ampoules were frozen while their stems were flame sealed. The ampoules were transferred to the sample chamber of a cryostat cooled with liquid nitrogen and the cryostat was placed in the sample chamber of the PRA system. The ampoule was allowed to equilibrate at a temperature indicated by a thermocouple for thirty minutes (the error is $\pm 1^\circ$ C).

Emission decay data were collected as a function of temperature. The emission lifetimes, τ_{em} (ns), for 2, c-1, and PP (the analogous open chain form of c-1) were plotted as a function of the temperature, T (K), and the plots are shown in Figure 3.5. In the top plot, τ_{em} vs. T is displayed for PP, whereas in the bottom plot τ_{em} vs. T is displayed for c-1. In each plot, τ_{em} vs. T is also displayed for 2.

The fit of the τ_{em} vs. T curve for 2 was done with a single monoexponential function, whereas the fits for PP and c-1 were done with a double exponential function. The activation parameters obtained from the fits of each of the complexes are shown in Table 3.1 [71a].

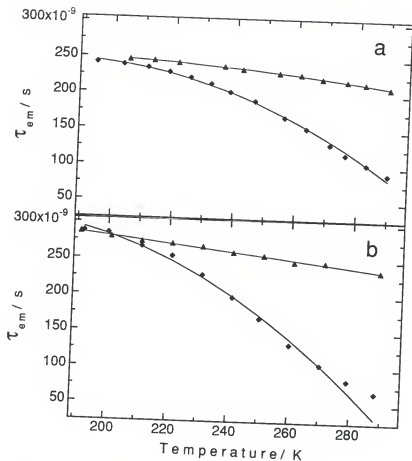


Figure 3.5. Low-temperature time-resolved emission experiments (lifetime, τ , ns versus temperature, K) of (a) PP (diamonds) and (bpy)ReI(CO)₃PyrCH₂Ph, PF₆⁻, where Pyr = 4-pyridine (triangles) and (b) c-1 (diamonds) and (bpy)ReI(CO)₃Pyr, PF₆⁻ (triangles) in 7/3 butyronitrile/acetonitrile.

Table 3.1. Activation parameters for photoinduced forward electron transfer obtained from low-temperature emission experiments for **PP** and **c-1**.

Complex	E_a (kcal/mol)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)
PP	5.9	5.0	-8
c-1	6.3	5.7	-5

Note: **PP** = (bpy)Re^I(CO)₃PyrCH₂NHCH(Ph)CH(Ph)Pip; Pyr = 4-pyridine and Pip = N-piperidine.

HPLC Chromatography

Quantitation of the quantum yield efficiency of *c*-1 $\rightarrow$ *t*-1 photoisomerization was done using HPLC. All products were injected onto a Whatman analytical ODS column and monitored at 270 nm. 2,2'-bipyridine was chosen as the internal standard for the quantum yield experiments and was added to a solution of [*c*-1] = 1.0×10^{-4} M (the absorbance at 366 nm, the photolysis wavelength, was 1) that had been photolyzed for approximately 20 seconds. The concentration of bipyridine in the final injection mixture was 9×10^{-5} M. The mobile phase consisted of an isocratic 77 % A/B mixture, in which A = 90 % CH₃CN/H₂O, 0.005 M sodium heptanesulfonic acid, and 0.05 M triethylamine, whereas B = 100 % H₂O, 0.005 M sodium heptanesulfonic acid, and 0.05 M triethylamine. The flow rate was kept at a constant 1.0 mL/minute.

Electrochemistry

Electrochemistry was performed with a cyclic voltammetry apparatus that used platinum working and auxiliary electrodes and a saturated calomel electrode (SCE) as the reference electrode. The experiments were done in CH₃CN with a 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The reduction potentials of the ligands of both *c*-1 and *t*-1 are shown in Table 3.2 and 3.3, respectively.

Table 3.2. The spectroscopic and electrochemical data for c-1, t-1, and 2a are listed below.

Compound	τ^a (ns)	ϕ_{em}^b	$E_{1/2}^c$ (V vs SSCE)	ϕ^d	ϕ^e
c-1	55	0.016	0.97	0.44 ± 0.05	-
t-1	233	0.057	1.24	-	0.48 ± 0.05
2a ^f	235	0.055	1.21	-	-

a The lifetimes were obtained in argon-degassed CH₃CN at room temperature.

b The quantum yields for emission, ϕ_{em} , were obtained in argon-degassed acetonitrile at room temperature. The actinometer for the quantum yields was Ru(bpy)₃²⁺ (Cl)₂ in air-saturated water ($\phi_{em} = 0.038$) [see Wang, Yingsheng, Ph.D. dissertation, University of Florida, 1994].

c All reduction potentials were obtained in CH₃CN with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. They were referenced vs SSCE at a scan rate of 200 mV/s.

d Quantum yield of disappearance (primarily c-1 → t-1).

e Quantum yield of appearance (t-1).

f See Chapter 2 for structure.

Table 3.3. The oxidation potentials for c-1 and t-1.

Scan Rate (mV/s)	Oxidation Potentials (V, SSCE)	
	c-1	t-1
25	+0.94	+1.15
50	+0.94	+1.16
75	+0.94	+1.10
100	+0.95	+1.20
150	+0.96	+1.22
175	+0.96	+1.22
200	+0.96	+1.24
250	+0.97	+1.25
300	+0.98	+1.26

Transient Absorption Spectra

Transient absorption spectra were obtained of solutions of c-1 and t-1 that had concentrations of 1.0×10^{-4} M in argon-degassed CH_3CN . The solutions were irradiated with 5 mJ laser pulses at 355 nm and the transient absorption was collected over a 500 ns window. Figure 3.6 displays the results of the transient absorption experiments. All transient absorption difference spectra were extracted by factor analysis of multiwavelength transient absorption kinetic data.

Discussion

Evidence for c-1 $\rightarrow$ t-1 Photoisomerization

The isomeric complexes c-1 and t-1 were synthesized and fully characterized. In both complexes, the near-UV absorption is dominated by the $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$ metal-to-ligand charge transfer (MLCT) transition of the Re chromophore [72]. Irradiation of a solution of c-1 in air-saturated or argon-degassed CH_3CN at 366 nm affords a single chemical product with high quantum efficiency. ^1H NMR, HPLC and high resolution mass spectral analysis of the photoproduct indicate that the photoprocess is c-1 $\rightarrow$ t-1 isomerization. In argon degassed solution c-1 $\rightarrow$ t-1 photoisomerization occurs with a quantum efficiency

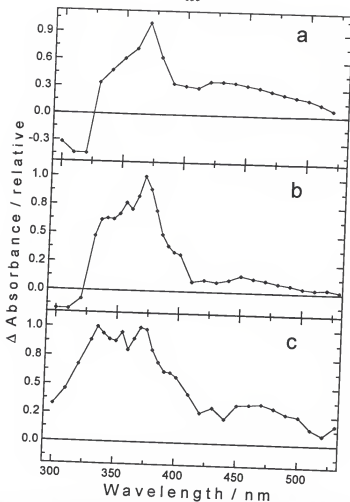


Figure 3.6. Transient absorption spectra of the principal spectral components extracted by factor analysis of multiwavelength transient absorption kinetic data in argon degassed CH_3CN . **a:** the only component for *t*-1 ($\tau = 247$ ns); **b:** first component observed for *c*-1 ($\tau_{\text{decay}} = 47$ ns); **c:** second component observed for *c*-1 ($\tau_{\text{rise}} = 47$ ns, $\tau_{\text{decay}} = 150$ ns).

of 0.46 ± 0.05 . Remarkably, irradiation of t-1 under the same conditions leads to no observable photochemical change.

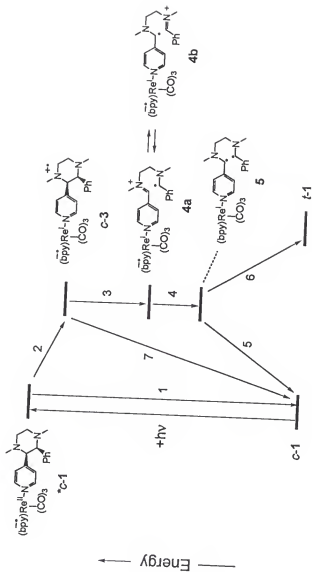
^1H NMR studies of the photolysis of a CDCl_3 solution of c-1 (see Figure 3.3) indicated the disappearance of c-1 with the concomitant evolution of a new product. The spectrum of the product was assigned to t-1 by comparison with the spectrum of an authentic sample of t-1. One of the most remarkable features of the spectra observed in Figure 3.3 is the lack of any other assignable products other than t-1. A mechanism for c-1 $\rightarrow$ t-1 photoisomerization is provided in Figure 3.7. Near-UV excitation of c-1 produces the MLCT excited state c-1*. The MLCT state relaxes either by radiative and non-radiative decay to c-1 (step 1) or by forward electron transfer (step 2) to afford charge separated state c-3 in which the piperazine donor is oxidized and the bpy acceptor ligand is reduced (e.g., $\text{bpy}^\bullet$).

Support for Electron Transfer in c-1*

Preliminary support for electron transfer in c-1* and not t-1* was obtained from calculations of ΔG_{FET} , the free energy for forward electron transfer, for both isomers. Since the following equation holds for ΔG_{FET} :

$$\Delta G_{\text{FET}} = E_{1/2}(\text{D}^+/\text{D}) - {}^*E_{1/2}(\text{Re}^+/\text{Re}^0) \quad (3-1)$$

Figure 3.7. Energy scheme depicting the photoisomerization of c-1.



where $D = c-1$ or $t-1$, and $E_{1/2}(c-1^+/c-1) = +0.96$ V, $E_{1/2}(t-1^+/t-1) = +1.24$ V, and $*E_{1/2}(Re^+/Re^0) = -1.22$ V (vs. SCE), ΔG_{FET} is exothermic only for $c-1^*$ (-250 mV vs. $+20$ mV for $t-1^*$). Thus, forward electron transfer should occur for $c-1^*$ and not $t-1^*$.

The occurrence of forward electron transfer (step 2 in Figure 3.7) in $c-1^*$ is directly supported by the fact that the MLCT emission lifetime of $c-1$ ($\tau_{em} = 55$ ns) is suppressed compared to that of model complex **2** ($\tau_{em} = 235$ ns). The emission lifetimes of $c-1^*$ and **2** allow estimation of k_2 (1.4×10^7 s $^{-1}$) and the quantum efficiency for formation of charge separated state $c-3$ ($\phi = 0.76$) [73]. Piperazine isomerization is believed to occur via fragmentation of the 2,3 C-C bond (step 3) to form a new charge separated state in which the piperazine exists as a distonic cation radical with two possible structures (**4a** or **4b**). Bond fragmentation in 1,2-diaminoethane radical cations is well preceded in acyclic systems [71, 74]. Indeed, recent studies indicate that for acyclic 1,2-diaryl-1,2-diaminoethanes such as **PP**, C-C bond fragmentation is exoergic and occurs with $k > 10^8$ s $^{-1}$ [74c]. Since C-C bond fragmentation in **4** is probably exoergic, the reverse process (e.g., $4 \rightarrow 3$) cannot occur, and therefore isomerization occurs via charge recombination (step 4) followed by coupling of 1,6-diradical **5** (step 6).

Low-temperature emission experiments also lent support to the occurrence of electron transfer in $c-1^*$ and not $t-1^*$. The data in Table 3.1 show that the

activation parameters for forward electron transfer for **c-1** and **PP** are very similar. Previous experiments have demonstrated that near-UV photolysis of **PP** leads to photochemical products as a result of electron transfer [71, 74]. The activation parameters for electron transfer in **c-1** and **PP** are within experimental error and imply that no significant differences exist between electron transfer in the open chain (**PP**) and the ring system, **c-1**; however, as a result of electron transfer in **c-1**, photoisomerization occurs to **t-1**. In **PP**, electron transfer in argon-degassed solution lead to photochemical products. As shown in Figure 3.3, however, photolysis of **c-1** resulted in almost complete conversion to **t-1** with no additional products.

Rationale for Absence of Electron Transfer in **t-1***

A significant question is why **t-1** $\rightarrow$ **c-1** photoisomerization does not occur. Quite remarkably, the MLCT emission lifetime of **t-1** ($\tau_{em} = 233$ ns) is *not* suppressed substantially from that of model 2, which indicates that forward electron transfer is too slow to compete with normal decay of the MLCT excited state, **t-1***. The lack of electron transfer quenching in **t-1*** precludes formation of charge separated state **t-3** (not shown in Figure 3.7), thereby closing off the pathway to **t-1** $\rightarrow$ **c-1** isomerization via fragmentation of the piperazine cation radical. Forward electron transfer is slower in **t-1** than in **c-1** because the *trans*

piperazine is more difficult to oxidize than the *cis* piperazine; indeed, the estimated driving force for step 2 is approximately -0.3 eV and 0 eV in c-1 and t-1, respectively.

Nanosecond transient absorption studies carried out on c-1 and t-1 provide evidence for the existence of the unique charge separated state 4. First, excitation of t-1 in degassed CH₃CN solution with a 10 ns, 355 nm pulse produces a single transient having a strong absorption band at 370 nm which is assigned to MLCT excited state t-1* (Figure 1a) [73c]. Factor analysis [75] of the transient absorption data indicates that t-1* decays with a lifetime of $\tau = 247$ ns, in accord with the emission lifetime. By contrast, excitation of c-1 under the same conditions affords a transient absorption spectrum that evolves with time; factor analysis indicates that the time-resolved absorption data is consistent with two absorbing transients. The first is clearly the MLCT state c-1*; the spectrum (Figure 3.6b) is very similar to that of t-1, and its decay lifetime (47 ns) is consistent with the MLCT emission lifetime of c-1. The second transient (Figure 3.6c), which is attributed to charge separated species 4, has rise and decay lifetimes of 247 and 150 ns, respectively. The assignment of the second transient to 4 is based on: (1) the similarity of its transient absorption spectrum to that observed for reactive intermediates produced by C-C bond fragmentation of acyclic diaminoethane cation radicals; [74] (2) the absence of an absorption band

at 600 nm which would be expected if the 1, 4-dimethylpiperazine cation radical is present [76].

Conclusion

Previous studies have examined the rates of charge recombination in structurally related (bpy)Re^I(CO)₃-D complexes, where D is an organic electron donor such as phenothiazine or N,N'-dimethylaniline [66-67]. These studies show that although the rate of charge recombination increases weakly with driving force or separation distance, in general, charge recombination in polar solvents occurs with $k \geq 5 \times 10^7 \text{ s}^{-1}$. Indeed, charge recombination rates less than 10^7 s^{-1} have only been achieved in metal complex based systems by using elaborate donor/acceptor "triad" assemblies [66c]. In view of this, it is remarkable that charge recombination in the charge separated state 4 is considerably slower (e.g., $k = 6.7 \times 10^6 \text{ s}^{-1}$) than in the related metal complex dyads. The basis for the comparatively long lifetime of the charge separated state lies in the fact that relaxation of 4 to c-1 (or t-1) involves diradical 5 as an intermediate. Thus, the rate determining step for decay of 4 involves an intramolecular electron transfer reaction (step 4) which is weakly exothermic ($\Delta G_4 \approx -0.2 \text{ eV}$) by virtue of the fact that the product (5) is a high energy intermediate. The low driving force for back electron transfer in charge separated state 4 is remarkable, since the driving force associated with

decay of charge separated states in typical dyads is highly exoergonic and lies within the Marcus inverted region [66, 77-78].

This study outlines a conceptually general means of increasing the lifetime of a charge separated state by coupling photoinduced electron transfer with a rapid, but reversible, chemical process. A similar concept has recently been successfully applied to increase the lifetime of the charge separated state in a porphyrin-quinone dyad by coupling electron transfer with a rapid proton transfer step [79].

Experimental

General Procedures

Solvents and chemicals used for synthesis were of reagent grade and were used without purification unless otherwise noted. 2,2'-bipyridine, benzyl cyanide, 4-pyridinecarboxaldehyde, selenium dioxide, ethylene diamine, pyridine, and *p*-toluenesulfonic acid were used as received. All organic compounds were purified by liquid chromatography on silica gel (230-400 mesh) and the transition metal complexes were purified by repeated precipitation from diethyl ether followed by repeated liquid chromatography on neutral alumina (Fisher, Brockman Grade III). Proton and carbon NMR spectra were obtained on a Gemini 300 MHz spectrophotometer. Refer to the synthetic scheme for compound acronyms.

Methyl isonicotinate. Isonicotinic chloride (Aldrich, 13.01 g, 100 mmol) was dissolved in 50 mL of ACS grade methanol and the solution was allowed to stir for about 2 hours at room temperature. The product was collected as a off-white solid after the solvent was removed by reduced pressure. It was washed several times with saturated sodium bicarbonate solution and extracted into 3 x 25 mL portions of methylene chloride. The organic layer was dried over anhydrous magnesium sulfate for 45 minutes. The solvent was filtered off and was removed under reduced pressure to give a white product, yield 12 g (85 %). *Spectral Data.* ^1H NMR (300 Mhz, CDCl_3) δ 4.41 (s, 3H), 7.68 (dd, 2H), 8.62 (d, 2H).

α -isonicotinoyl benzyl cyanide [80-81]. An ethanolic solution of sodium ethoxide was prepared by dissolving sodium spheres (Aldrich, 5-8 mm diameter, 1.86 g, 81 mmol) into 25 mL of ethanol. The solution was kept under a blanket of argon during the course of the reaction. After 40 minutes, the sodium spheres had completely dissolved in the ethanol at which point **2** (12 g, 85 mmol) and benzyl cyanide (13.5 g, 131 mmol) were added to the solution. The solution became yellow and viscous and was stirred by a mechanical stirrer. The reaction was allowed to reflux at 76° C for about 3 hours. After cooling, the thick reaction mixture was poured into 100 mL of distilled water and the aqueous solution was extracted into 3 x 50 mL portions of diethyl ether to remove unreacted starting materials. The basic aqueous layer was subsequently neutralized by addition of

several hundred mL of 5 M HCl whereupon a yellow solid precipitated. After insuring that the pH was less than 5, a yellow solid was collected on a Buechner funnel and dried overnight in vacuo. After drying, **3** was collected as a yellow solid, yield 11.9 g (64 %). **3** is insoluble in most NMR solvents and was used immediately for the next step without characterization.

1-phenyl-2-(4-pyridyl)ethanone [80-81]. To a 1 L round bottom filled with 600 mL of concentrated HCl, 12.3 g of **3** (55 mmol) was added and the reaction was allowed to reflux overnight ($\approx$ 12 hours). Most of the HCl was removed under reduced pressure and 400 mL of saturated sodium bicarbonate was added to the remaining brown-yellow solid to obtain a pH > 8. The resulting aqueous solution was extracted by 3 x 50 mL portions of methylene chloride. The organic layers were combined and dried over MgSO₄ for 10 minutes and removed under reduced pressure to afford **4** as a pale yellow solid, yield 5.7 g (53 %). *Spectral Data.* ¹H NMR (300 MHz, CDCl₃) δ 4.55 (s, 2H), 6.99 - 7.50 (m, 5H), 7.75 (dd, 2H), 8.75 (d, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 46.8 (methylene), 122.6, 143.5, 152.0 (pyridyl), 128.3, 129.9, 130.5, 134.3 (phenyl), 198.0 (carbonyl).

1-phenyl-2-(4-pyridyl)ethanedione [82]. **4** (3 g, 15 mmol) was placed in a 1 L round bottom flask to which 25 mL of glacial acetic acid was added followed

by 2.1 g (20 mmol) of SeO_2 and the reaction was stirred by means of a mechanical stirbar. The reaction temperature was maintained between 40 and 50° C for 40 minutes after which time TLC (silica, 2% $\text{MeOH}/\text{CHCl}_3$) indicated the disappearance of the starting material at $R_f = 0.20$ and the appearance of a spot at $R_f = 0.65$ that was ascribed to **5**. The acetic acid was removed by reduced pressure to leave **5** as a thick, red oil which was dissolved in several mL of 2 % $\text{MeOH}/\text{CHCl}_3$ and eluted through a 3 inch deep by 2 inch wide silica column in a fritted funnel in order to eliminate most of the red selenium impurities. Despite the elution, upon solvent removal it was noticed that some of the selenium impurities remained. Refluxing **5** in ethanol helped to precipitate most of the selenium impurities which were removed by gravity filtration and centrifugation. These last purification steps were repeated as needed until no selenium precipitates could be observed. **5** was recovered in good yield, 2.5 g (80 %). *Spectral Data.* ^1H NMR (300 MHz, CDCl_3) δ 7.55 (t, 2H), 7.70 (t, 1H), 7.80 (d, 2H), 8.00 (d, 2H), 8.88 (d, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 123.6, 140.2, 151.7, (pyridyl), 130.3, 131.1, 133.3, 136.5 (phenyl), 193.5, 193.8 (carbonyls).

2-phenyl-3-(4-pyridyl)-5,6-dihydropyrazine [82] **5** (0.20 g, 1.0 mmol) was dissolved in 75 mL of benzene and 0.56 g (1.0 mmole) of ethylene diamine was added whereupon the solution became cloudy. The solution was allowed to reflux in a Dean-Stark apparatus for 2 hours while TLC (silica gel, 5%

MeOH/CH₂Cl₂) was used to monitor the reaction progress. A new spot was observed after an hour at an R_f of 0.3 although much of the starting material remained at R_f = 0.6. The reaction was accelerated by adding 5-fold excess of ethylene diamine (2.8 g, 50 mmole) since it was observed that during the course of the reaction, ethylene diamine distills into the Dean-Stark trap. After another 1 hour, the spot at R_f = 0.6 completely disappeared leaving only the product spot at R_f = 0.3. The benzene was removed under reduced pressure to give a white solid which was dried in vacuo, yield 0.24 g (100%). *Spectral Data.* ¹H NMR (300 MHz, CDCl₃) δ 3.75 (s, 4H), 7.34 (m, 7H), 8.60 (d, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 45.5, 46.3 (methylenes), 123.9, 143.3, 149.8 (pyridyl), 127.7, 128.3, 128.7, 129.6 (phenyl), 129.2 (2-methine), 130.1 (3-methine).

2-phenyl-3-(4-pyridyl)piperazine [83]. In a typical procedure, 0.14 g (0.60 mmol) of 6 was dissolved in 10 mL of methanol and kept under a nitrogen blanket. The solution was stirred and cooled to -30° C by using an isopropanol/dry ice bath and sodium cyanoborohydride (0.73 g, 1.2 mmol) was added. A 2 mL methanol solution of pyridinium sulfonate was made up by combining separate 1 mL methanolic solutions of pyridine (0.08 g, 1.0 mmol) and *p*-toluenesulfonic acid (0.19 g, 1 mmol). The pyridinium sulfonate buffer solution was then added to the chilled solution and the solution instantly became scarlet in color. Samples for TLC analysis (5% MeOH/CH₂Cl₂) were removed from the solution at regular

intervals while the solution was maintained over a temperature range of -30 to -40° C. The TLC samples were extracted into methylene chloride after addition of several drops of a 12 N NaOH solution (the pH was typically > 9). After 1 hour, the starting material spot at $R_f = 0.4$ vanished leaving a low, cone-shaped, strongly streaking spot at $R_f = 0.1$ which was attributed to **7**. The reaction was allowed to warm to room temperature and the methanol was removed under reduced pressure. A red precipitate was obtained which was dissolved into 10 mL of methylene chloride and 15 mL of 12 N NaOH. A thick emulsion developed which was cleared up by adding 5 mL of saturated saline solution. A fluffy, whitish precipitate was observed in the organic layer that was redissolved by adding 10 mL of methylene chloride. **7** was reextracted at least two more times until the organic layer was colorless in appearance. The organic layer was dried over magnesium sulfate, evaporated under reduced pressure, and kept in vacuo for 20 hours. Note that column chromatography (silica) could not be used to purify **7** since it adheres so strongly to silica limiting recovery yields to $< 5\%$ of **7**. **7** was obtained as a brown liquid, yield 0.14 g (98 %). This procedure yields **7** as a 1:1 mixture of *cis* and *trans* diastereomers. *Spectral Data.* ^1H NMR (300 MHz, CDCl_3) δ 2.15 (s, 2H, amines), 2.85 - 3.35 (m, 8H, methylenes), 3.60 - 3.70 (dd, 2H, *trans* methines, 9 Hz), 4.2 - 4.3 (dd, 2H, *cis* methines, $J = 4$ Hz), 6.85 - 7.4 (m, 12 H), 8.2 - 8.63 (m, 4H).

N,N'-dimethyl-2-phenyl-3-(4-pyridyl)piperazine [84]. **7** (0.14 g, 0.59 mmol) was dissolved in 10 mL of dry THF and 0.2 g (6.7 mmol) of paraformaldehyde was added to the solution. The resulting suspension was allowed to stir under nitrogen while 0.15 g (4.0 mmol) of sodium borohydride (Aldrich, 0.4 g tablets) was added as a powder. The suspension began to assume a turbid color as it was stirring and became black after 15 minutes. Trifluoroacetic acid (5 mL) was added drop-wise by means of an addition funnel to the solution over a period of 30 minutes. Over this time, it was noticed that the dark solution became clear and eventually assumed a transparent yellow color. After 1 hour, TLC samples (silica, 6% MeOH/CH₂Cl₂ eluant, collected as described above for **7**) showed that although a new spot at $R_f = 0.5$ appeared, the spot for **7** ($R_f = 0.1$) did not completely disappear, so an additional 0.2 g (5.3 mmol, half a tablet) of NaBH₄ was added to the solution. After another hour, the starting material was still not consumed, so 0.4 g (11 mmol) of NaBH₄ was added to the solution and TLC analysis showed the reaction was completed. The total mass of NaBH₄ used for the reaction was 0.9 g (24 mmol). Again, liquid chromatography was not applicable for **8** since it like **7** also adhered strongly to a silica column. The solution was poured into 50 mL of 12 N NaOH and extracted into 3 portions of 50 mL methylene chloride. The organic layers were combined, dried over magnesium sulfate and filtered to give a thick, orange-brown oil, yield 0.08 g (50%). The product is a mixture of the cis and trans diastereomers in approximately 1:1 ratio.

Spectral Data. ^1H NMR (300 MHz, CDCl_3) δ 2.01 - 2.07 (set of 4 singlets, 6H, methyls), 2.5 - 3.2 (m, 6H, methines and methylenes), 6.5 - 8.5 (m, 9H, aromatics); GC/El: m/z = 267.080, calc'd = 267.410.

Separation of *cis*-9 and *trans*-9. Semi-preparative reversed phaseHPLC was chosen to separate *cis*-9 and *trans*-9. All separations were performed on an ODS-3 Partisil Magnum 9 semi-prep column using a Rainin Dynamax dual-head HPLC system. An isocratic mobile phase consisting of 60 % methanol/water with 0.01 M triethylamine was used at a flow rate of 2.5 mL/min and detection wavelength of 254 nm. At these particular conditions, *trans*-8 came off at 11.4 minutes while *cis*-8 came off at 16.5 minutes. In a typical procedure, 100 mg was dissolved in 500 μL of methanol and 50 μL aliquots (10 mg of 8) were injected onto the column for each run. The individual fractions were collected immediately as they came off and stored in separate containers. This procedure was repeated until 50 mg of each isomer was obtained. The stereochemistry of the isomers was established by comparing the observed m.p's and ^1H NMR spectra of *cis*-8 and *trans*-8 with those of the corresponding isomers of 1,4-dimethyl-2,3-diphenylpiperazine [85]. *Data for cis*-8. m.p. 86°C . ^1H NMR (300 MHz, CDCl_3) δ 2.15 (s, 3H), 2.20 (s, 3H), 2.81 (m, 2H), 3.20 (m, 2H), 3.90 (d, 2H), 7.20 - 7.32

(m, 7H), 8.35 (d, 2H). Data for *trans*-8: δ 2.07 (s, 3H), 2.13 (s, 3H), 2.81 (m, 2H), 3.08 (dd, 2H), 3.20 (t, 2H), 6.4 - 7.8 (m, 7H), 8.33 (d, 2H).

General Synthetic Procedure for *cis*-9 and *trans*-9.

Preparation of (bpy)Re(CO)₃OSO₂CF₃.

(bpy)Re(CO)₃Cl (0.13 g, 0.28 mmol) was suspended in 5 mL of freshly distilled methylene chloride (distilled from CaH₂ pellets) and to this suspension was carefully and slowly added 0.25 mL (4.2 mmol) of trifluoromethanesulfonic acid (Aldrich). Immediately the suspension became a clear yellow solution which was allowed to stir at room temperature for 40 minutes. 50 mL of diethyl ether was then added to the solution which after about 1 minute developed a thick, pale precipitate that was collected and washed with excess ether over a medium porosity sintered glass funnel. The product recovered was light yellow, yield 0.11 g (68%).

Synthesis of *cis*-9 and *trans*-9.

cis-9. *cis*-8 (0.045 g, 0.17 mmol) was weighed out into a 50 mL round bottom and dissolved with 5 mL of freshly distilled, dry THF (Na/K, benzophenone). Freshly prepared (bpy)Re(CO)₃OSO₂CF₃ (0.055 g, 0.1 mmol) and 0.21 g (1.3 mmol) of NH₄PF₆ were then added to the solution and TLC

(alumina, 10 % $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$) was used to monitor the reaction which was stirred at room temperature under nitrogen for 14 hours. After 14 hours, the product, *cis*-9 showed a bright yellow cone-shaped spot at $R_f = 0.5$. *Cis*-9 was precipitated out of 25 mL of diethyl ether while stirring to remove any excess ligands and collected on a medium porosity sintered glass funnel. Further purification was effected by chromatography on alumina (10% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$). After purification, the final product was recovered as a white microcrystalline solid, yield 0.03 g (40 %). *Spectral Data.* ^1H NMR (300 MHz, CD_3CN) δ 1.96 (s, 3H, buried in CD_3CN), 2.16 (s, 3H), 2.40 - 3.1 (m, 4H), 3.47 (d, 1H, $J = 4.5$ Hz), 3.61 (d, 1H, $J = 4.5$ Hz), 6.89 (d, 2H), 7.02 (t, 2H), 7.15 (d, 2H), 7.75 (m, 2H), 7.87 (d, 2H), 8.31 (m, 4H), 9.17 (t, 2H); ^{13}C NMR (75 MHz, CD_3CN) δ 40.3 (1-methyl), 42.8 (4-methyl), 50.4 (5-methylene), 53.2 (6-methylene), 69.7 (2-methine), 70.9 (3-methine), 123.2, 140.0, 149.7 (pyridyl), 127.5, 128.3, 128.6, 130.2 (phenyl), 139.2, 152.4, 153.0 (bipyridyl); POS, $M + 1$, CS/FAB: 694.1813, calc'd: 694.1830.

***trans*-9.** The compound was prepared exactly as described above for *cis*-9, except *trans*-8 was used in place of *cis*-8. *Spectral Data.* ^1H NMR (300 MHz, CD_3CN) δ 2.1 (s, 3H, buried in CD_3CN), 2.16 (s, 3H), 2.40 (m, 2H), 2.94 (d, 2H), 2.61 (d, 1H, $J = 8.7$ Hz), 2.90 (d, 1H, $J = 8.7$ Hz), 7.07 (s, 2H), 7.2 - 7.6 (broad s, 2H), 7.42 (t, 2H), 7.84 (t, 1H), 7.92 (t, 1H), 8.12 (d, 2H), 8.50 (m, 4H), 9.22 (d,

1H), 9.35 (d, 1H); ¹³C NMR (75 MHz, CD₃CN) δ 41.3 (1-methyl), 42.2 (4-methyl), 51.4 (5-methylene), 54.3 (6-methylene), 70.0 (2-methine), 71.8 (3-methine), 124.3, 141.0, 151.6 (pyridyl), 125.9, 128.6, 128.9, 129.7 (phenyl), 140.9, 153.5, 153.6 (bipyridyl); POS, M + 1, CS/FAB: 694.1754, calc'd: 694.1830.

APPENDIX

Introduction

[ReC₁₈H₁₃N₃O₃][Co(CO)₄], $M_r = 676.48$, Monoclinic, $P2_1/c$, $a = 8.554$ (1) Å, $b = 28.807$ (4) Å, $c = 19.498$ (3) Å, $b = 97.86$ (1)°, $V = 4759$ (1) Å³, $Z = 8$, $D_{\text{calc.}} = 1.888$ g cm⁻³, Mo K α ($\lambda = 0.71073$ Å), $T = 298$ K. Data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing MoK α radiation ($\lambda = 0.71073$ Å). 40 reflections with $20.0^\circ \leq 2\theta \leq 22.0^\circ$ were used to refine the cell parameters. 9185 reflections were collected using the ω -scan method. Four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was $< 2\%$). Absorption corrections were applied based on measured crystal faces using *SHELXTL plus* [86]; absorption coefficient, $\mu = 5.83$ mm⁻¹ (min. and max. transmission factors are 0.395 and 0.568, respectively).

The structure was solved by the heavy-atom method in *SHELXTL plus* from which the location of the Re and Co atoms were obtained. The rest of the non-hydrogen atoms were obtained from a subsequent difference Fourier map. The structure was refined in *SHELXTL plus* using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the positions of the hydrogen atoms were calculated in ideal positions and their isotropic thermal parameters were fixed. 613 parameters were refined and $\sum w(\Delta F_o)^2$ was minimized; $w = 1/(\sigma(\Delta F_o)^2)$, $\sigma(F_o) = 0.5 \text{ kl}^{-1/2} \{ [s(I)]^2 + (0.02I)^2 \}^{1/2}$, $I(\text{intensity}) = (I_{\text{peak}} - I_{\text{background}})(\text{scan rate})$, and $s(I) = (I_{\text{peak}} + I_{\text{background}})^{1/2}(\text{scan rate})$, k is the correction due to decay and L_p effects, 0.02 is a factor used to down weight intense reflections and to account for instrument instability. The linear absorption coefficient was calculated from values from the

International Tables for X-ray Crystallography [87]. Scattering factors for non-hydrogen atoms were taken from Cromer & Mann [88] with anomalous-dispersion corrections from Cromer & Liberman [89], while those of hydrogen atoms were from Stewart, Davidson & Simpson [90].

Experimental

Table A.1: Crystallographic data for 2.

A. Crystal data (298 K)		Compound 2	
a , Å		8.554 (1)	
b , Å		28.807 (4)	
c , Å		19.498 (3)	
β , deg.		97.86 (1)	
V , Å ³		4759 (1)	
d_{calc} , g cm ⁻³ (298 K)		1.888	
Empirical formula		[ReC ₁₈ H ₁₃ N ₃ O ₃][Co(CO) ₄]	
Formula wt, g		676.48	
Crystal system		Monoclinic	
Space group		P 2 ₁ /c	
Z		8	
$F(000)$, electrons		2592	
Crystal size (mm ³)		0.42 x 0.15 x 0.11	
B. Data collection (298 K)			
Radiation, λ (Å)		Mo-K α , 0.71073	
Mode		w-scan	
Scan range		Symmetrically over 1.2 ∞ about K $\alpha_{1,2}$	
maximum			
Background		offset 1.0 and -1.0 in w from K $\alpha_{1,2}$	
		maximum	
Scan rate, deg. min. ⁻¹		3 – 6	
2 θ range, deg.		3 – 50	
Range of $h\ k\ l$		0	$\leq h \leq 10$
		0	$\leq k \leq 34$
		-22	$\leq l \leq 22$
Total reflections measured		9185	
Unique reflections		8377	
Absorption coeff. μ (Mo-K α), mm ⁻¹		5.83	
Min. & Max. Transmission		0.395, 0.568	

Table A.1 -- continued

C. Structure refinement

S, Goodness-of-fit	1.53
Reflections used, $I > 3\sigma(I)$	4398
No. of variables	613
R, wR* (%)	5.66, 5.61
R _{int} (%)	3.20
Max. shift/esd	0.0001
min. peak in diff. four. map ($e \text{ \AA}^{-3}$)	-1.12
max. peak in diff. four. map ($e \text{ \AA}^{-3}$)	1.78

* Relevant expressions are as follows, where in the footnote F_O and F_C represent, respectively, the observed and calculated structure-factor amplitudes.

Function minimized was $w(|F_O| - |F_C|)^2$, where $w = (s(F))^{-2}$

$$R = \hat{A}(|F_O| - |F_C|) / \hat{A}|F_O|$$

$$wR = [\hat{A}w(|F_O| - |F_C|)^2 / \hat{A}|F_O|^2]^{1/2}$$

$$S = [\hat{A}w(|F_O| - |F_C|)^2 / (m-n)]^{1/2}$$

Table A.2: Fractional coordinates and equivalent isotropic^a thermal parameters ($\text{\AA}^2$) for the non-H atoms of compound 2.

Atom	x	y	z	U
Re	0.09648(8)	0.21213(2)	0.43456(4)	0.0394(2)
N1	0.092(2)	0.1387(4)	0.4080(7)	0.044(5)
N2	0.334(2)	0.1870(5)	0.4716(6)	0.039(5)
N3	0.185(2)	0.2219(5)	0.3341(7)	0.050(6)
O1	0.136(2)	0.3141(5)	0.4728(8)	0.092(7)
O2	-0.246(2)	0.2364(5)	0.3745(7)	0.082(6)
O3	-0.011(2)	0.2007(5)	0.5770(7)	0.074(6)
C1	-0.034(2)	0.1154(7)	0.3774(10)	0.064(8)
C2	-0.033(3)	0.0706(8)	0.3614(11)	0.076(9)
C3	0.109(3)	0.0466(8)	0.3747(12)	0.092(11)
C4	0.241(3)	0.0683(7)	0.4081(10)	0.073(9)
C5	0.233(2)	0.1159(6)	0.4247(8)	0.042(6)
C6	0.363(2)	0.1425(6)	0.4584(8)	0.041(6)
C7	0.512(2)	0.1235(7)	0.4807(9)	0.062(8)
C8	0.628(3)	0.1507(9)	0.5141(10)	0.074(10)
C9	0.596(2)	0.1971(7)	0.5275(9)	0.052(7)
C10	0.446(2)	0.2138(6)	0.5054(9)	0.054(7)
C11	0.321(2)	0.2469(6)	0.3313(11)	0.057(8)
C12	0.365(3)	0.2566(8)	0.2664(13)	0.082(10)
C13	0.286(3)	0.2404(9)	0.2080(13)	0.089(12)
C14	0.154(3)	0.2132(8)	0.2118(13)	0.091(11)
C15	0.105(2)	0.2055(7)	0.2754(10)	0.070(9)
C16	0.129(2)	0.2768(6)	0.4583(11)	0.058(8)
C17	-0.118(2)	0.2283(6)	0.3954(9)	0.052(7)
C18	0.030(2)	0.2034(6)	0.5216(10)	0.053(7)
Co	0.2138(3)	0.06476(9)	0.63181(14)	0.0615(11)
O4	0.344(2)	0.1580(6)	0.6464(10)	0.110(9)
O5	-0.070(2)	0.0697(7)	0.5321(10)	0.134(10)
O6	0.113(2)	0.0323(6)	0.7591(8)	0.098(7)
O7	0.442(3)	0.0037(8)	0.5852(12)	0.176(13)
C19	0.295(3)	0.1205(10)	0.6389(12)	0.083(11)
C20	0.044(3)	0.0677(8)	0.5706(12)	0.084(11)
C21	0.153(2)	0.0447(7)	0.7081(11)	0.069(9)
C22	0.348(3)	0.0247(9)	0.6010(13)	0.096(12)
Re'	0.35576(8)	-0.09723(2)	0.08436(4)	0.0416(2)
N1'	0.122(2)	-0.0689(5)	0.0587(7)	0.044(5)
N2'	0.365(2)	-0.0319(5)	0.1400(6)	0.041(5)

Table A.2 -- continued

Atom	x	y	z	U
N3'	0.260(2)	-0.1212(5)	0.1782(7)	0.046(6)
O1'	0.692(2)	-0.1318(5)	0.1375(8)	0.091(7)
O2'	0.294(2)	-0.1899(5)	0.0102(7)	0.090(7)
O3'	0.4641(14)	-0.0545(4)	-0.0441(6)	0.053(5)
C1'	0.002(2)	-0.0871(6)	0.0150(8)	0.047(7)
C2'	-0.148(2)	-0.0700(6)	0.0070(9)	0.050(7)
C3'	-0.180(2)	-0.0329(6)	0.0431(9)	0.052(7)
C4'	-0.056(2)	-0.0116(6)	0.0876(8)	0.044(7)
C5'	0.090(2)	-0.0309(6)	0.0956(8)	0.045(7)
C6'	0.222(2)	-0.0095(6)	0.1393(9)	0.044(6)
C7'	0.212(2)	0.0291(6)	0.1800(8)	0.055(7)
C8'	0.345(2)	0.0477(7)	0.2170(10)	0.065(8)
C9'	0.490(2)	0.0269(7)	0.2148(10)	0.068(9)
C10'	0.495(2)	-0.0138(6)	0.1774(9)	0.053(7)
C11'	0.336(2)	-0.1124(7)	0.2416(10)	0.065(8)
C12'	0.268(3)	-0.1187(8)	0.2998(10)	0.082(10)
C13'	0.123(3)	-0.1407(9)	0.294(2)	0.097(13)
C14'	0.057(3)	-0.1519(8)	0.2315(15)	0.089(11)
C15'	0.123(2)	-0.1416(6)	0.1740(11)	0.059(8)
C16'	0.571(2)	-0.1199(7)	0.1186(9)	0.058(8)
C17'	0.320(3)	-0.1553(7)	0.0382(10)	0.066(9)
C18'	0.424(2)	-0.0724(6)	0.0043(10)	0.045(7)
Co'	0.6511(3)	0.15929(8)	0.19167(12)	0.0531(9)
O4'	0.899(2)	0.0992(7)	0.1555(10)	0.142(10)
O5'	0.544(2)	0.1367(7)	0.3223(8)	0.120(9)
O6'	0.378(2)	0.1513(7)	0.0867(10)	0.150(10)
O7'	0.748(2)	0.2551(6)	0.1928(11)	0.128(10)
C19'	0.800(3)	0.1211(8)	0.1695(12)	0.079(10)
C20'	0.590(2)	0.1453(7)	0.2700(11)	0.071(9)
C21'	0.484(3)	0.1548(7)	0.1269(11)	0.087(10)
C22'	0.713(2)	0.2176(8)	0.1932(11)	0.071(9)

^aFor anisotropic atoms, the U value is U_{eq} , calculated as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ where A_{ij} is the dot product of the i^{th} and j^{th} direct space unit cell vectors.

Table A.3: Bond Lengths (Å) and Angles (°) for the non-H atoms of compound 2.

1	2	3	1-2	1-2-3
N1	Re	N2	2.177(13)	75.0(5)
N1	Re	N3		84.8(5)
N1	Re	C16		172.6(6)
N1	Re	C17		98.9(6)
N2	Re	N3	2.185(13)	85.4(5)
N2	Re	C16		98.2(6)
N2	Re	C17		173.7(6)
N2	Re	C18		92.2(6)
N3	Re	C16	2.21(2)	91.9(7)
N3	Re	C17		92.2(6)
N3	Re	C18		177.6(6)
C16	Re	C17	1.93(2)	87.8(7)
C16	Re	C18		88.0(8)
C17	Re	C18	1.94(2)	90.2(8)
C18	Re	N1	1.88(2)	95.0(6)
C1	N1	C5	1.34(2)	119.7(14)
C1	N1	Re		125.2(12)
C5	N1	Re	1.37(2)	115.0(10)
C6	N2	C10	1.34(2)	120.7(14)
C6	N2	Re		116.3(10)
C10	N2	Re	1.33(2)	123.0(11)
C11	N3	C15	1.38(2)	119.(2)
C11	N3	Re		119.7(12)
C15	N3	Re	1.34(2)	121.2(13)
C16	O1		1.11(2)	
C17	O2		1.14(2)	
C18	O3		1.19(3)	
C2	C1	N1	1.33(3)	124.(2)
C3	C2	C1	1.39(3)	118.(2)
C4	C3	C2	1.37(3)	120.(2)
C5	C4	C3	1.41(3)	119.(2)
C6	C5	N1	1.44(2)	117.1(15)
C6	C5	C4		124.(2)
N1	C5	C4		119.(2)
C7	C6	N2	1.40(3)	120.(2)
C7	C6	C5		123.(2)
N2	C6	C5		116.5(15)

Table A.3 -- continued

1	2	3	1-2	1-2-3
C8	C7	C6	1.36(3)	120.(2)
C9	C8	C7	1.40(3)	120.(2)
C10	C9	C8	1.38(2)	118.(2)
N2	C10	C9		122.(2)
C12	C11	N3	1.40(3)	119.(2)
C13	C12	C11	1.33(3)	122.(2)
C14	C13	C12	1.39(4)	119.(2)
C15	C14	C13	1.38(3)	119.(2)
N3	C15	C14		122.(2)
Re	C16	O1		175.(2)
Re	C17	O2		177.(2)
Re	C18	O3		176.(2)
C19	Co	C20	1.75(3)	107.0(11)
C19	Co	C21		113.5(10)
C20	Co	C21	1.75(2)	106.3(11)
C20	Co	C22		108.3(11)
C21	Co	C22	1.74(2)	110.7(11)
C22	Co	C19	1.79(3)	110.6(12)
C19	O4		1.16(3)	
C20	O5		1.15(3)	
C21	O6		1.15(3)	
C22	O7		1.08(4)	
Co	C19	O4		176.(2)
Co	C20	O5		178.(2)
Co	C21	O6		179.(2)
Co	C22	O7		172.(2)
N1'	Re'	N2'	2.156(13)	75.9(5)
N1'	Re'	N3'		82.8(5)
N1'	Re'	C16'		173.4(6)
N1'	Re'	C17'		98.0(7)
N2'	Re'	N3'	2.169(13)	81.3(5)
N2'	Re'	C16'		98.6(6)
N2'	Re'	C17'		172.5(8)
N2'	Re'	C18'		95.2(6)
N3'	Re'	C16'	2.213(14)	92.8(7)
N3'	Re'	C17'		93.6(7)
N3'	Re'	C18'		174.9(6)
C16'	Re'	C17'	1.98(2)	87.2(8)
C16'	Re'	C18'		91.4(7)

Table A.3 -- continued

1	2	3	1-2	1-2-3
C17'	Re'	C18'	1.90(2)	89.4(8)
C18'	Re'	N1'	1.88(2)	92.8(6)
C1'	N1'	C5'	1.35(2)	117.2(14)
C5'	N1'		1.36(2)	
C6'	N2'	C10'	1.38(2)	119.4(14)
C10'	N2'		1.35(2)	
C11'	N3'	C15'	1.34(2)	117.(2)
C15'	N3'		1.31(2)	
C16'	O1'		1.10(2)	
C17'	O2'		1.14(2)	
C18'	O3'		1.16(2)	
C2'	C1'	N1'	1.36(3)	124.(2)
C3'	C2'	C1'	1.33(3)	119.(2)
C4'	C3'	C2'	1.41(2)	119.(2)
C5'	C4'	C3'	1.36(2)	119.(2)
C6'	C5'	N1'	1.46(2)	117.(2)
C6'	C5'	C4'		122.(2)
N1'	C5'	C4'		121.3(15)
N2'	C6'	C5'		115.1(14)
C9'	C8'		1.39(3)	
C10'	C9'	C8'	1.39(3)	118.(2)
N2'	C10'	C9'		122.(2)
C12'	C11'	N3'	1.36(3)	123.(2)
C13'	C12'	C11'	1.38(4)	118.(2)
C14'	C13'	C12'	1.31(4)	117.(3)
C15'	C14'	C13'	1.36(4)	123.(2)
N3'	C15'	C14'		121.(2)
C19'	Co'	C20'	1.78(2)	112.5(10)
C19'	Co'	C21'		108.4(10)
C20'	Co'	C21'	1.73(2)	107.4(10)
C20'	Co'	C22'		109.5(10)
C21'	Co'	C22'	1.78(2)	107.0(10)
C22'	Co'	C19'	1.76(2)	111.7(10)
C19'	O4'		1.11(3)	
C20'	O5'		1.17(3)	
C21'	O6'		1.12(3)	
C22'	O7'		1.12(3)	
Co'	C19'	O4'		176.(2)

Table A.3 -- continued

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
Co'	C20'	O5'		177.(2)
Co'	C21'	O6'		179.(2)
Co'	C22'	O7'		178.(2)

Table A.4: Anisotropic thermal parameters for the non-H atoms of compound 2.

Atom	U11	U22	U33	U12	U13	U23
Re	0.0365(4)	0.0353(4)	0.0453(4)	0.0016(4)	0.0019(3)	-0.0010(3)
N1	0.056(10)	0.027(8)	0.047(9)	-0.011(7)	-0.002(8)	-0.000(6)
N2	0.039(8)	0.045(9)	0.030(8)	-0.009(7)	-0.004(6)	-0.006(7)
N3	0.057(10)	0.032(9)	0.057(10)	0.009(8)	-0.001(8)	-0.003(7)
O1	0.094(12)	0.047(10)	0.120(13)	0.016(9)	-0.034(9)	-0.023(9)
O2	0.046(9)	0.111(13)	0.084(10)	0.032(9)	-0.012(8)	-0.023(9)
O3	0.066(10)	0.095(12)	0.066(9)	0.011(8)	0.024(8)	0.007(8)
C1	0.057(13)	0.049(13)	0.08(2)	0.001(11)	-0.009(11)	-0.007(11)
C2	0.07(2)	0.06(2)	0.10(2)	-0.014(13)	0.002(13)	-0.027(13)
C3	0.12(2)	0.048(14)	0.11(2)	-0.02(2)	0.01(2)	-0.031(13)
C4	0.10(2)	0.041(13)	0.078(15)	0.016(12)	0.009(13)	-0.000(11)
C5	0.033(10)	0.053(12)	0.035(10)	0.004(9)	-0.009(8)	0.001(8)
C6	0.049(11)	0.052(12)	0.022(9)	-0.011(10)	0.002(8)	0.010(8)
C7	0.073(15)	0.065(14)	0.044(12)	0.014(12)	-0.005(11)	0.020(10)
C8	0.07(2)	0.10(2)	0.050(13)	0.035(15)	0.004(12)	0.036(13)
C9	0.021(10)	0.08(2)	0.054(12)	-0.005(9)	-0.005(9)	0.014(10)
C10	0.061(13)	0.041(11)	0.061(12)	0.013(11)	0.016(11)	0.001(10)
C11	0.041(12)	0.046(12)	0.08(2)	-0.008(10)	0.005(11)	0.002(11)
C12	0.08(2)	0.08(2)	0.09(2)	0.034(14)	0.04(2)	0.03(2)
C13	0.11(2)	0.10(2)	0.06(2)	0.03(2)	0.04(2)	-0.002(15)
C14	0.13(2)	0.07(2)	0.07(2)	0.01(2)	0.01(2)	0.001(14)
C15	0.077(15)	0.08(2)	0.049(13)	0.006(12)	-0.005(12)	-0.001(12)
C16	0.049(12)	0.028(11)	0.089(15)	-0.007(9)	-0.015(11)	-0.003(10)
C17	0.067(13)	0.051(12)	0.039(11)	0.010(10)	0.012(10)	-0.008(9)
C18	0.049(12)	0.050(13)	0.055(12)	-0.009(9)	-0.013(10)	-0.013(10)
Co	0.073(2)	0.049(2)	0.063(2)	0.0132(15)	0.012(2)	0.0058(14)
O4	0.097(14)	0.074(12)	0.15(2)	-0.008(11)	0.002(12)	0.007(12)
O5	0.15(2)	0.14(2)	0.102(15)	0.001(15)	-0.020(13)	0.026(13)
O6	0.105(13)	0.126(15)	0.064(10)	-0.011(11)	0.018(9)	0.026(10)
O7	0.17(2)	0.17(2)	0.21(2)	0.09(2)	0.09(2)	-0.02(2)
C19	0.08(2)	0.11(2)	0.07(2)	0.02(2)	0.020(13)	0.01(2)
C20	0.12(2)	0.054(15)	0.08(2)	-0.01(2)	0.01(2)	0.002(13)
C21	0.08(2)	0.060(14)	0.066(14)	-0.003(12)	-0.004(13)	-0.009(12)
C22	0.10(2)	0.10(2)	0.10(2)	0.01(2)	0.04(2)	0.01(2)
Re'	0.0451(4)	0.0358(4)	0.0450(4)	0.0043(4)	0.0098(3)	0.0044(3)
N1'	0.044(9)	0.033(8)	0.053(9)	-0.005(7)	-0.002(7)	-0.006(7)
N2'	0.053(9)	0.047(9)	0.022(7)	-0.003(8)	-0.006(7)	-0.004(6)
N3'	0.072(11)	0.033(8)	0.034(9)	0.003(8)	0.011(8)	0.016(7)

Table A.4 – continued

Atom	U11	U22	U33	U12	U13	U23
O1'	0.062(10)	0.087(12)	0.123(14)	0.043(9)	0.005(10)	0.019(10)
O2'	0.16(2)	0.042(9)	0.078(10)	0.006(10)	0.034(10)	-0.008(8)
O3'	0.071(9)	0.045(8)	0.046(7)	0.001(7)	0.017(7)	0.012(6)
C1'	0.059(12)	0.034(11)	0.045(11)	-0.007(9)	0.003(10)	-0.008(8)
C2'	0.048(12)	0.047(12)	0.050(11)	-0.005(10)	-0.015(9)	0.002(9)
C3'	0.044(12)	0.050(12)	0.064(13)	-0.011(10)	0.019(10)	0.005(10)
C4'	0.053(12)	0.033(10)	0.050(11)	0.005(9)	0.017(9)	-0.003(8)
C5'	0.067(13)	0.040(11)	0.032(9)	-0.011(10)	0.019(9)	-0.001(8)
C6'	0.047(11)	0.029(10)	0.054(11)	-0.001(9)	-0.004(9)	-0.007(8)
C7'	0.073(14)	0.045(12)	0.046(11)	0.006(10)	0.000(10)	-0.012(9)
C8'	0.061(14)	0.055(13)	0.077(14)	-0.002(11)	0.003(12)	-0.038(11)
C9'	0.07(2)	0.065(15)	0.068(14)	-0.010(12)	-0.001(12)	-0.012(12)
C10'	0.045(11)	0.048(12)	0.060(12)	-0.009(10)	-0.008(10)	0.007(10)
C11'	0.058(13)	0.08(2)	0.057(14)	0.003(11)	0.010(12)	0.020(11)
C12'	0.12(2)	0.09(2)	0.040(12)	0.00(2)	0.015(14)	0.011(12)
C13'	0.10(2)	0.09(2)	0.11(2)	0.04(2)	0.07(2)	0.06(2)
C14'	0.06(2)	0.09(2)	0.12(2)	-0.006(13)	0.03(2)	0.05(2)
C15'	0.053(13)	0.047(12)	0.081(15)	-0.013(10)	0.021(11)	0.029(11)
C16'	0.068(14)	0.058(13)	0.045(11)	0.014(11)	-0.004(11)	0.019(10)
C17'	0.12(2)	0.036(12)	0.049(12)	-0.001(12)	0.034(12)	0.017(10)
C18'	0.033(10)	0.038(11)	0.062(12)	0.009(8)	0.001(9)	-0.009(10)
Co'	0.059(2)	0.046(2)	0.052(2)	0.0037(13)	-0.0012(13)	-0.0083(12)
O4'	0.12(2)	0.14(2)	0.16(2)	0.082(14)	0.011(13)	-0.053(14)
O5'	0.13(2)	0.17(2)	0.060(10)	-0.059(13)	0.029(11)	-0.004(11)
O6'	0.14(2)	0.14(2)	0.14(2)	0.048(13)	-0.092(14)	-0.074(14)
O7'	0.14(2)	0.063(12)	0.18(2)	-0.027(11)	0.013(13)	-0.003(12)
C19'	0.056(14)	0.07(2)	0.11(2)	-0.002(12)	-0.002(13)	-0.019(14)
C20'	0.08(2)	0.07(2)	0.064(15)	-0.015(12)	-0.004(13)	-0.032(12)
C21'	0.12(2)	0.06(2)	0.07(2)	0.030(15)	-0.021(15)	-0.030(12)
C22'	0.08(2)	0.054(14)	0.08(2)	-0.014(13)	0.012(12)	-0.008(13)

Note: Uij are the mean-square amplitudes of vibration in Å² from the general temperature factor expression

$$\exp[-2\pi^2(h^2a^*2U11 + k^2b^*2U22 + l^2c^*2U33 + 2hka^*b^*U12 + 2hla^*c^*U13 + 2klb^*c^*U23)]$$

Table A.5: Fractional coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the H atoms of compound 2.

Atom	x	y	z	U
H1	-0.13176	0.13216	0.36632	0.08
H2	-0.127530	0.05517	0.34114	0.08
H3	0.11507	0.01482	0.36061	0.08
H4	0.33803	0.05138	0.41997	0.08
H7	0.53161	0.0913	0.47245	0.08
H8	0.73087	0.13799	0.52841	0.08
H9	0.676(2)	0.2169(7)	0.5513(9)	0.08
H10	0.42194	0.24554	0.514690	0.08
H11	0.38382	0.2574	0.37298	0.08
H12	0.45657	0.27569	0.26403	0.08
H13	0.32008	0.2473	0.16418	0.08
H14	0.09775	0.19975	0.1706	0.08
H15	0.01019	0.18795	0.2774	0.08
H1'	0.02316	-0.11366	-0.01203	0.08
H2'	-0.22924	-0.08448	-0.02447	0.08
H3'	-0.28556	-0.02084	0.03908	0.08
H4'	-0.07572	0.016280	0.11209	0.08
H7'	0.11086	0.04318	0.18238	0.08
H8'	0.33723	0.07511	0.24434	0.08
H9'	0.58498	0.04039	0.23864	0.08
H10'	0.59386	-0.0297	0.17806	0.08
H11'	0.44279	-0.10123	0.24601	0.08
H12'	0.31941	-0.10814	0.34392	0.08
H13'	0.07316	-0.14744	0.33411	0.08
H14'	-0.0424	-0.16795	0.22624	0.08
H15'	0.06767	-0.14944	0.129330	0.08

Table A.6: Bond Lengths (Å) and Angles ($^{\circ}$) of the H atoms of compound 2.

1	2	3	1-2	1-2-3
H1	C1	C2	0.96(2)	118.(2)
H1	C1	N1		118.(2)
H2	C2	C3	0.96(2)	121.(2)
H2	C2	C1		121.(2)
H3	C3	C4	0.96(2)	120.(2)
H3	C3	C2		120.(2)
H4	C4	C5	0.96(2)	121.(2)
H4	C4	C3		121.(2)
H7	C7	C8	0.96(2)	120.(2)
H7	C7	C6		120.(2)
H8	C8	C9	0.96(2)	120.(2)
H8	C8	C7		120.(2)
H9	C9	C10	0.96(2)	121.(2)
H9	C9	C8		121.(2)
H10	C10	N2	0.96(2)	119.(2)
H10	C10	C9		119.(2)
H11	C11	C12	0.96(2)	121.(2)
H11	C11	N3		121.(2)
H12	C12	C13	0.96(2)	119.(3)
H12	C12	C11		119.(2)
H13	C13	C14	0.96(3)	121.(2)
H13	C13	C12		121.(3)
H14	C14	C15	0.96(2)	120.(3)
H14	C14	C13		120.(3)
H15	C15	N3	0.96(2)	119.(2)
H15	C15	C14		119.(2)
H1'	C1'	C2'	0.96(2)	118.(2)
H1'	C1'	N1'		118.(2)
H2'	C2'	C3'	0.96(2)	120.(2)
H2'	C2'	C1'		120.(2)
H3'	C3'	C4'	0.96(2)	121.(2)
H3'	C3'	C2'		121.(2)
H4'	C4'	C5'	0.96(2)	120.(2)
H4'	C4'	C3'		120.(2)
H8'	C8'	C9'	0.96(2)	120.(2)
H9'	C9'	C10'	0.96(2)	121.(2)
H9'	C9'	C8'		121.(2)
H10'	C10'	N2'	0.96(2)	119.(2)
H10'	C10'	C9'		119.(2)

Table A.6 -- continued

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
H11'	C11'	C12'	0.96(2)	119.(2)
H11'	C11'	N3'		119.(2)
H12'	C12'	C13'	0.96(2)	121.(2)
H12'	C12'	C11'		121.(2)
H13'	C13'	C14'	0.96(3)	121.(3)
H13'	C13'	C12'		121.(3)
H14'	C14'	C15'	0.96(2)	119.(2)
H14'	C14'	C13'		119.(3)
H15'	C15'	N3'	0.96(2)	119.(2)
H15'	C15'	C14'		119.(2)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S			
1	0	0	539	540	12	6	5	0	110	-141-110	5 11	0	479	-440	60	5 17	0	1239	1206	36	4 24	0	134	-168-134		
2	0	0	739	-767	16	7	5	0	123	81-123	6 11	0	180	197	33	6 17	0	981	-1015	54	5 24	0	705	-747	66	
3	0	0	215	218	16	8	5	0	382	472-100	7 11	0	840	171	53	7 17	0	774	-674	60	6 24	0	702	-898	70	
4	0	0	379	-392	21	9	5	0	139	199-139	8 11	0	109	461	53	8 17	0	150	220-150	74	7 24	0	256	151-256		
5	0	0	1587	-1574	21	10	6	0	457	-411	9 11	0	123	81-123	9 17	0	721	801	35	8 24	0	466	-139	72		
6	0	0	203	-28-203	27	11	6	0	759	-757	20	0	159	-109	30	1 18	0	519	358	52	9 25	0	1147	-198	43	
7	0	0	2026	-2020	27	12	6	0	1402	1338	17	1 12	0	3075	-2716	20	2 18	0	503	-152	58	10 25	0	1004	-154	46
8	0	0	732	761	48	13	6	0	564	-496	32	2 12	0	1170	-1134	24	3 18	0	321	-311-321	71	11 25	0	522	-771	82
9	0	0	962	987	49	14	6	0	433	503	51	3 12	0	2048	2020	22	4 18	0	530	-413	73	12 25	0	749	632	69
10	0	0	144	85-144	51	15	6	0	371	-389	-69	4 12	0	389	328	74	5 18	0	479	-203	88	13 25	0	1653	-109	31
1	1	0	352	-356	19	16	6	0	628	541	56	5 12	0	1688	1627	28	6 18	0	580	-242	71	14 25	0	194	-321	184
2	1	0	1794	-1553	15	17	6	0	420	-400-100	7 12	0	154	-296	72	7 18	0	145	-56-145	45	15 25	0	356	-226	72	
3	1	0	919	-889	-57	18	6	0	257	-288-257	8 12	0	140	104	184-144	8 18	0	130	-421	27	16 25	0	358	-889	137	
4	1	0	293	-289	-57	19	6	0	2913	-2830	18	9 12	0	100	-265	150	9 18	0	611	600	45	17 25	0	625	620	77
5	1	0	913	-853	27	20	7	0	145	-2-145	10 12	0	3889	3818	24	10 18	0	328	-441	111	18 25	0	516	191	-99	
6	1	0	1323	1317	26	21	7	0	795	-795	25	11 12	0	2139	2073	22	11 18	0	130	-42	130	19 25	0	334	558	140
7	1	0	875	883	41	22	7	0	542	-517	39	12 12	0	1731	1689	26	12 18	0	614	581	66	20 25	0	536	372	73
8	1	0	954	979	51	23	7	0	1083	1113	30	13 12	0	1206	-1214	33	13 18	0	575	600	82	21 25	0	1370	1321	40
9	1	0	147	6-147	57	24	7	0	879	-788	38	14 12	0	469	-585	41	14 18	0	438	268	102	22 25	0	592	484	75
10	1	0	2093	-1982	12	25	7	0	126	-9-126	15 12	0	811	-808	55	15 18	0	1352	1066	30	23 25	0	354	-151	137	
1	2	0	293	-170	40	26	7	0	450	633-104	16 12	0	3514	-1521	41	16 18	0	1352	1363	28	24 25	0	156	-332	156	
2	2	0	436	-371	34	27	7	0	467	-441	-97	17 12	0	148	350	48	17 18	0	179	77	119	25 25	0	108	729	47
3	2	0	1182	1190	20	28	7	0	227	-293	65	18 12	0	1946	1900	20	18 18	0	1612	121	29	26 25	0	111	246	41
4	2	0	1337	1515	22	29	7	0	210	-255	18	19 12	0	1416	1330	24	19 18	0	511	86	211	28 25	0	485	-417	-97
5	2	0	1189	1253	28	30	7	0	687	-685	26	20 12	0	1382	-1819	24	20 18	0	575	576	66	29 25	0	586	-609	84
6	2	0	118	-192	-18	31	7	0	887	853	25	21 12	0	116	-301	16	21 18	0	780	756	64	30 25	0	908	-017	51
7	2	0	431	-7	-82	32	7	0	512	465	41	22 12	0	1198	-1126	35	22 18	0	335	325	186	31 25	0	1088	-103	48
8	2	0	296	-411	-203	33	7	0	211	-2-211	41	23 12	0	1198	-1126	35	23 18	0	335	325	186	32 25	0	1088	-103	48
9	2	0	691	-583	68	34	7	0	339	362	-98	24 12	0	1648	-1580	33	24 18	0	437	253	61	33 25	0	1008	-103	48
10	2	0	2883	2749	13	35	7	0	129	-30-129	56	25 12	0	148	-62	148	25 18	0	905	815	41	34 25	0	638	-715	69
1	3	0	918	-871	18	36	7	0	136	-4-136	74	26 12	0	352	341-13	41	26 18	0	506	141	84	35 25	0	136	182	-36
2	3	0	4796	4495	19	37	7	0	472	-191	50	27 12	0	452	-220	15	27 18	0	539	-552	72	36 25	0	756	182	-36
3	3	0	2334	2311	21	38	7	0	94	-228	94	28 12	0	352	-203	15	28 18	0	506	141	84	37 25	0	653	-433	71
4	3	0	1705	-1674	22	39	7	0	3884	3183	20	29 12	0	2290	-2279	24	29 18	0	345	2784	74	38 25	0	622	581	79
5	3	0	199	91	-199	40	7	0	292	55	-66	30 12	0	1047	-1049	30	30 18	0	587	782	74	39 25	0	464	-157	-106
6	3	0	597	-524	56	41	7	0	252	-220	93	31 12	0	552	-482	57	31 18	0	801	-816	44	40 25	0	543	210	76
7	3	0	177	-1256	35	42	7	0	1361	1369	27	32 12	0	778	-872	48	32 18	0	903	-916	44	41 25	0	380	307	-138
8	3	0	130	216	-138	43	7	0	848	-737	41	33 12	0	817	723	53	33 18	0	925	428	12	42 25	0	331	345	30
9	3	0	512	-235	-97	44	7	0	560	-632	70	34 12	0	663	656	68	34 18	0	903	-916	44	43 25	0	1351	12	-151
10	3	0	175	-1567	12	45	7	0	140	-214	-140	35 12	0	353	488	72	35 18	0	585	-585	119	44 25	0	1019	1104	50
1	4	0	372	3275	14	46	7	0	656	-496	74	36 12	0	325	498	198	36 18	0	514	583	83	45 25	0	1019	1104	50
2	4	0	828	760	19	47	7	0	10	0	1027	37 12	0	2797	-2756	22	37 18	0	514	583	83	46 25	0	1019	1104	50
3	4	0	3119	-3073	21	48	7	0	1027	985	21	38 12	0	2797	-2756	22	38 18	0	514	583	83	47 25	0	1019	1104	50

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S			
4	4	0	736	199	30	2	10	0	948	953	24	1	16	0	346	238	54	
5	4	0	1098	1100	27	3	10	0	1147	1148	25	2	16	0	740	652	38	
6	4	0	1387	1470	27	4	10	0	1533	1566	24	3	16	0	1482	1170	26	
7	4	0	568	583	59	5	10	0	1737	1772	38	4	16	0	925	997	42	
8	4	0	138	271	138	6	10	0	277	297	138	5	16	0	909	924	42	
9	4	0	136	66	136	7	10	0	869	800	49	6	16	0	414	451	98	
10	4	0	710	703	72	8	10	0	540	439	78	7	16	0	1062	1111	32	
11	5	0	3124	2980	16	9	10	0	562	363	81	8	16	0	557	534	56	
12	5	0	447	1384	16	1	11	0	344	323	54	9	16	0	1069	1041	27	
13	5	0	444	502	39	2	11	0	254	2569	20	10	16	0	771	2821	28	
14	5	0	375	142	175	3	11	0	2393	2303	21	11	16	0	383	526	65	
15	5	0	432	362	55	4	11	0	871	871	33	12	16	0	536	665	61	
16	5	0	409	361	51	5	11	0	1411	1386	42	13	16	0	630	727	67	
17	5	0	582	592	30	6	11	0	1244	1261	34	14	16	0	1005	937	71	
18	5	0	1832	1733	16	7	11	0	1347	1353	38	15	16	0	595	519	78	
19	5	0	1145	1057	16	8	11	0	1045	1060	32	16	16	0	484	288	86	
20	5	0	1392	1398	11	9	11	0	488	429	47	17	16	0	203	195	203	
21	5	0	2534	2568	11	10	11	0	93	2	93	18	17	16	1	1339	1281	30
22	5	0	210	172	59	11	11	0	1246	1167	20	19	16	0	104	345	108	
23	5	0	938	901	19	12	11	0	1631	1563	17	20	16	0	1045	1060	27	
24	5	0	2068	2104	19	13	11	0	1863	1808	14	21	16	0	2153	2138	20	
25	5	0	816	873	30	14	11	0	3911	3733	82	22	16	0	1474	1404	18	
26	5	0	1866	903	34	15	11	0	515	550	19	23	16	0	2189	2170	17	
27	5	0	189	124	189	16	11	0	3518	3361	17	24	16	0	1731	2593	60	
28	5	0	648	638	57	17	11	0	743	701	24	25	16	0	1428	1411	18	
29	5	0	312	242	157	18	11	0	2999	2679	21	26	16	0	1351	358	46	
30	5	0	147	324	147	19	11	0	879	989	37	27	16	0	838	827	25	
31	5	0	300	111	218	20	11	0	307	325	124	28	16	0	982	952	23	
32	5	0	376	290	123	21	11	0	415	501	88	29	16	0	2011	1977	24	
33	5	0	1356	1412	35	22	11	0	415	501	88	30	16	0	1408	1444	30	
34	5	0	230	234	230	23	11	0	937	957	50	31	16	0	1548	1586	69	
35	5	0	376	274	73	24	11	0	149	82	149	32	16	0	746	672	59	
36	5	0	1517	1634	22	25	11	0	1242	1216	43	33	16	0	231	328	23	
37	5	0	1630	1651	20	26	11	0	502	482	80	34	16	0	144	60	44	
38	5	0	79	89	79	27	11	0	144	321	60	35	16	0	1464	1417	30	
39	5	0	220	277	78	28	11	0	144	321	60	36	16	0	251	208	251	
40	5	0	421	4347	147	29	11	0	2078	2048	23	37	16	0	1780	1795	44	
41	5	0	668	762	102	30	11	0	1269	1233	22	38	16	0	1761	1724	24	
42	5	0	3613	3575	11	31	11	0	1457	1360	19	39	16	0	1473	1462	24	
43	5	0	2633	2441	15	32	11	0	1817	1746	16	40	16	0	1387	1323	45	
44	5	0	2176	2063	17	33	11	0	1397	1413	98	41	16	0	1540	1513	31	
45	5	0	1493	1431	19	34	11	0	4617	4419	28	42	16	0	15901	15647	19	
46	5	0	783	808	31	35	11	0	1284	255	42	43	16	0	1300	112	70	
47	5	0	409	361	51	36	11	0	1411	1386	42	44	16	0	630	727	67	
48	5	0	582	592	30	37	11	0	1244	1261	34	45	16	0	1005	937	71	
49	5	0	1832	1733	16	38	11	0	1347	1353	38	46	16	0	595	519	78	
50	5	0	1145	1057	16	39	11	0	1045	1060	32	47	16	0	484	288	86	
51	5	0	1392	1398	11	40	11	0	488	429	47	48	16	0	203	195	203	
52	5	0	2534	2568	11	41	11	0	93	2	93	49	16	0	1339	1281	30	
53	5	0	210	172	59	42	11	0	1246	1167	20	50	16	0	104	345	108	
54	5	0	938	901	19	43	11	0	1631	1563	17	51	16	0	1045	1060	27	
55	5	0	2068	2104	19	44	11	0	1863	1808	14	52	16	0	2153	2138	20	
56	5	0	816	873	30	45	11	0	3911	3733	82	53	16	0	1474	1404	18	
57	5	0	1866	903	34	46	11	0	515	550	19	54	16	0	2189	2170	17	
58	5	0	189	124	189	47	11	0	3518	3361	17	55	16	0	1731	2593	60	
59	5	0	648	638	57	48	11	0	743	701	24	56	16	0	1428	1411	18	
60	5	0	312	242	157	49	11	0	2999	2679	21	57	16	0	1351	358	46	
61	5	0	147	324	147	50	11	0	879	989	37	58	16	0	838	827	25	
62	5	0	300	111	218	51	11	0	307	325	124	59	16	0	2011	1977	24	
63	5	0	376	290	123	52	11	0	415	501	88	60	16	0	1408	1444	30	
64	5	0	1356	1412	35	53	11	0	415	501	88	61	16	0	1548	1586	69	
65	5	0	230	234	230	54	11	0	937	957	50	62	16	0	746	672	59	
66	5	0	376	274	73	55	11	0	149	82	149	63	16	0	231	328	23	
67	5	0	1517	1634	22	56	11	0	1242	1216	43	64	16	0	144	60	44	
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69	5	0	79	89	79	58	11	0	144	321	60	66	16	0	251	208	251	
70	5	0	421	4347	147	59	11	0	2078	2048	23	67	16	0	1780	1795	44	
71	5	0	668	762	102	60	11	0	1269	1233	22	68	16	0	1761	1724	24	
72	5	0	3613	3575	11	61	11	0	1457	1360	19	69	16	0	1473	1462	24	
73	5	0	2633	2441	15	62	11	0	1817	1746	16	70	16	0	1387	1323	45	
74	5	0	2176	2063	17	63	11	0	1397	1413	98	71	16	0	1540	1513	31	
75	5	0	1493	1431	19	64	11	0	4617	4419	28	72	16	0	15901	15647	19	
76	5	0	783	808	31	65	11	0	1284	255	42	73	16	0	1300	112	70	
77	5	0	409	361	51	66	11	0	1411	1386	42	74	16	0	630	727	67	
78	5	0	582	592	30	67	11	0	1244	1261	34	75	16	0	1005	937	71	
79	5	0	1832	1733	16	68	11	0	1347	1353	38	76	16	0	595	519	78	
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81	5	0	1392	1398	11	70	11	0	488	429	47	78	16	0	203	195	203	
82	5	0	2534	2568	11	71	11	0	93	2	93	79	16	0	1339	1281	30	
83	5	0	210	172	59	72	11	0	1246	1167	20	79	16	0	104	345	108	
84	5	0	938	901	19	73	11	0	1631	1563	17	80	16	0	1045	1060	27	
85	5	0	2068	2104	19	74	11	0	1863	1808	14	81	16	0	2153	2138	20	
86	5	0	816	873	30	75	11	0	3911	3733	82	82	16	0	1474	1404	18	
87	5	0	1866	903	34	76	11	0	515	550	19	83	16	0	2189	2170	17	
88	5	0	189	124	189	77	11	0	3518	3361	17	84	16	0	1731	2593	60	
89	5	0	648	638	57	78	11	0	743	701	24	85	16	0	1428	1411	18	
90	5	0	312	242	157	79	11	0	2999	2679	21	86	16	0	1351	358	46	
91	5	0	147	324	147	80	11	0	879	989	37	87	16	0	838	827	25	
92	5	0	300	111	218	81	11	0	307	325	124	88	16	0	2011	1977	24	
93	5	0	376	290	1													

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S
6	2	1	1030	1095	31	2	5	1	3961	3800	18	1	8	1	800	754	22
7	2	1	534	-549	58	3	5	1	372	232	43	2	8	1	372	232	43
8	2	1	1040	-1097	40	3	5	1	3319	3258	18	2	8	1	1057	-835	23
9	2	1	450	202	-91	3	5	1	851	-580	20	2	11	1	1549	1531	19
10	2	1	512	512	-102	3	5	1	225	-122	-139	3	11	1	1091	1055	25
-9	3	1	143	347	-143	3	5	1	454	785	35	3	11	1	1524	1494	25
-8	3	1	131	158	-131	3	5	1	1275	1260	35	4	11	1	113	126	-113
-7	3	1	120	223	-120	3	5	1	387	-415	-104	5	11	1	364	-115	-103
-6	3	1	893	-806	34	3	5	1	156	-36	-146	6	11	1	1188	-164	41
-5	3	1	1260	-1195	23	3	5	1	306	326	-217	7	11	1	400	506	-119
-4	3	1	361	-498	35	3	5	1	501	515	82	8	11	1	148	31	-148
-3	3	1	174	-1565	17	3	5	1	982	912	38	9	11	1	459	-485	-115
-2	3	1	675	-634	21	3	5	1	1255	1277	30	10	11	1	575	426	78
-1	3	1	1580	1536	12	3	5	1	107	8	-107	11	11	1	692	-561	57
0	3	1	1303	1832	49	3	5	1	362	305	37	12	11	1	139	-215	-129
1	3	1	2387	2272	13	3	5	1	2311	-2197	20	13	11	1	183	1759	26
2	3	1	3724	3638	16	3	5	1	1848	-1659	18	14	11	1	857	907	38
3	3	1	85	-9	-85	3	5	1	1133	-1137	17	15	11	1	124	1173	24
4	3	1	210	-12	-112	3	5	1	1891	-1865	30	16	11	1	2260	2271	20
5	3	1	723	-640	34	3	5	1	408	371	31	17	11	1	1848	-1827	19
6	3	1	1251	-1237	29	3	5	1	2093	2720	18	18	11	1	1833	1814	48
7	3	1	613	-550	50	3	5	1	1150	1090	40	19	11	1	511	-564	35
8	3	1	132	-138	-132	3	5	1	1333	1326	23	20	11	1	2184	-2159	21
9	3	1	394	47	-104	3	5	1	2269	2226	22	21	11	1	1231	1230	24
10	4	1	452	-39	-105	3	5	1	681	-710	44	22	11	1	255	-221	-14
						7	6	1	409	-537	-92	23	11	1	1395	-1356	39
						7	6	1	689	726	75	24	11	1	347	-411	-44
						7	6	1	806	775	48	25	11	1	1107	-1094	53
						7	6	1	806	775	48	26	11	1	1107	-1094	53
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						7	6	1	806	775	48	98	11	1	1107	-1094	53

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S
6 16	1	294	-202-184	-6 20	1	503	566 95	3 23	1	135	20-125	4 27	1	419	353-114
7 16	1	641	-405 68	-5 20	1	135	-50-135	5 23	1	671	619 82	5 27	1	380	-305-133
8 16	1	145	-243-145	-4 20	1	677	717 56	6 23	1	931	528 59	6 27	1	318	-16-566
-8 17	1	377	199-141	-3 20	1	1118	-1081 35	7 23	1	583	257 73	-5 28	1	808	-693 59
-7 17	1	553	486 83	-2 20	1	1955	-1893 27	7 23	1	313	273-13	-4 28	1	907	723 58
-6 17	1	1300	-1145 42	-1 20	1	1223	-1219 29	-7 24	1	351	-45-134	-3 28	1	465	316 58
-5 17	1	1040	-973 41	0 20	1	883	-892 48	-6 24	1	256	250-236	-2 28	1	288	54-211
-4 17	1	547	-524 64	1 20	1	713	733 43	-5 24	1	726	746 63	-1 28	1	172	1170 41
-3 17	1	1676	-1665 26	2 20	1	1353	1335 31	-4 24	1	719	-510 52	1 28	1	586	-471 80
-2 17	1	473	432 53	3 20	1	235	262-235	-3 24	1	296	-531-135	2 28	1	442	-427 85
-1 17	1	651	510 43	4 20	1	1234	1183 36	-2 24	1	264	39-223	3 28	1	412	465-124
0 17	1	104	-22 73	5 20	1	959	913 48	-1 24	1	1436	-111 32	4 28	1	145	-165-145
1 17	1	2303	2256 23	6 20	1	570	-461 81	0 24	1	146	289-105	5 28	1	148	160-148
2 17	1	1308	1532 27	7 20	1	344	-211-193	1 24	1	492	159 63	6 28	1	435	-22-134
3 17	1	114	7-14	8 20	1	716	-667 73	2 24	1	134	-267 34	-5 29	1	41	221-131
4 17	1	220	-143-220	-8 21	1	535	271 95	3 24	1	139	1410 36	-4 29	1	20	580
5 17	1	1210	-1172 37	-7 21	1	339	-489-138	4 24	1	138	204-128	-3 29	1	430	-317-107
6 17	1	747	-746 62	-6 21	1	450	332 94	5 24	1	327	-211-35	-2 29	1	458	-448 98
7 17	1	142	-24-142	-5 21	1	1155	-1140 40	6 24	1	559	620 52	-1 29	1	356	-437 84
8 17	1	510	-494-100	-4 21	1	934	-948 46	7 24	1	429	-51-129	0 29	1	853	-882 54
-8 18	1	968	-938 55	-3 21	1	126	381-136	-5 25	1	793	-630 63	1 29	1	213	-171-293
-7 18	1	292	-413-292	-2 21	1	1203	-115 34	-4 25	1	353	363 80	2 29	1	402	-144-122
-6 18	1	349	-502-156	-1 21	1	1101	957 32	-3 25	1	376	43-110	3 29	1	469	-377 98
-5 18	1	1533	-1430 33	0 21	1	2417	2416 18	-2 25	1	1139	1266 70	4 29	1	359	514-143
-4 18	1	1778	1698 30	1 21	1	118	-148-118	-3 25	1	546	605 76	5 29	1	166	97-146
-3 18	1	1352	1324 30	2 21	1	1332	1345 34	1 25	1	453	162 80	6 29	1	403	-144-122
-2 18	1	277	-4-104	3 21	1	873	778 41	0 25	1	128	1500 38	7 29	1	965	-974 57
-1 18	1	2401	2375 25	4 21	1	1337	-1276 35	-1 25	1	304	-355-139	8 29	1	482	-505-106
0 18	1	697	697 40	5 21	1	366	-116-117	2 25	1	137	-21-133	9 29	1	301	-196-198
1 18	1	1195	-1096 29	6 21	1	874	-728 53	3 25	1	814	644 33	0 30	1	816	805 66
2 18	1	116	51-116	7 21	1	1068	-112 52	4 25	1	160	-118 61	1 30	1	401	356-125
3 18	1	2914	-2810 27	-7 22	1	1018	-1052 57	5 25	1	945	-460 85	2 30	1	394	358-143
4 18	1	1384	-1336 32	-6 22	1	624	-581 78	6 25	1	130	-95-150	3 30	1	1063	-1015 32
5 18	1	507	376 70	-5 22	1	624	525 65	-6 26	1	150	135-143	4 30	1	351	402-166
6 18	1	651	-619 71	-4 22	1	416	-247 93	-5 26	1	362	37-114	-3 31	1	455	-411-117
7 18	1	318	51-204	-3 22	1	832	838 40	-4 26	1	412	-118 95	-2 31	1	142	-49-142
8 18	1	608	727 86	-2 22	1	1577	1551 30	-3 26	1	133	101-133	-1 31	1	142	-49-142
-8 19	1	136	-190-156	-1 22	1	336	-44 97	-2 26	1	133	101-133	-1 31	1	142	-49-142

[illegible]

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S
0	4	2	114	-50	-57	-3	7	2	1168	-1131	21	-4	10	2	1166	-1125	25
1	4	2	2992	2937	15	-2	7	2	824	-787	21	-3	10	2	1130	1137	24
-2	16	2	2385	2567	23	3	19	2	1149	-1119	34	-5	23	2	842	830	57
-1	16	2	459	-520	59	4	19	2	433	263	-98	-4	23	2	922	-969	48
0	16	2	920	-893	21	5	19	2	219	65	-219	-1	23	2	676	590	38
1	16	2	189	-303	-189	6	19	2	689	-678	65	-2	23	2	434	-244	-82
2	16	2	244	-244	24	7	19	2	677	673	71	-1	23	2	1353	-937	28
3	16	2	338	-436	-82	8	19	2	405	130	-119	0	23	2	701	805	40
4	16	2	982	916	37	8	20	2	252	-170	-252	1	23	2	323	-278	-111
5	16	2	680	-523	52	7	20	2	147	-181	-147	2	23	2	867	-829	38
6	16	2	987	917	47	-6	20	2	749	610	58	3	23	2	1556	1325	32
7	16	2	846	835	55	-5	20	2	731	708	52	4	23	2	229	91	-229
8	16	2	378	-77	-126	-4	20	2	335	5	-124	5	23	2	225	203	-225
-8	17	2	275	-138	-275	-3	20	2	850	850	42	6	23	2	945	993	59
-7	17	2	956	965	55	-2	20	2	1229	-1283	31	7	23	2	661	-574	72
-6	17	2	370	-321	-106	-1	20	2	271	254	-144	-7	24	2	150	230	-150
-5	17	2	170	-176	41	0	20	2	468	-478	46	-6	24	2	604	-601	31
-4	17	2	832	704	41	1	20	2	1132	-1187	32	-5	24	2	138	-48	-138
-3	17	2	735	-773	42	2	20	2	917	976	40	-4	24	2	581	-466	65
-2	17	2	632	-689	44	3	20	2	443	330	-76	-3	24	2	1114	-1144	10
-1	17	2	107	-378	-107	4	20	2	395	-259	-97	-2	24	2	330	400	-136
0	17	2	1415	-1416	23	5	20	2	945	945	47	-1	24	2	607	-430	-58
1	17	2	398	-772	-67	6	20	2	398	-205	-119	0	24	2	408	-4	-134
2	17	2	788	842	40	7	20	2	542	-459	-91	1	24	2	1791	172	32
3	17	2	248	197	-134	8	20	2	152	318	-152	2	24	2	934	855	50
4	17	2	1255	1199	32	-8	21	2	148	-78	-148	3	24	2	596	99	-248
5	17	2	474	699	-80	-7	21	2	334	-233	-166	4	24	2	572	528	74
6	17	2	401	-320	-116	-6	21	2	290	-17	-206	5	24	2	575	-596	77
7	17	2	223	209	-223	-5	21	2	132	-83	-132	6	24	2	628	-494	76
8	17	2	439	-169	-111	-4	21	2	288	-3	-154	7	24	2	152	-233	-152
-8	18	2	401	274	-128	-3	21	2	580	421	59	-6	25	2	767	-667	64
-7	18	2	362	272	-146	-2	21	2	553	470	62	-5	25	2	144	-22	-144
-6	18	2	305	234	-114	-1	21	2	118	202	-118	-4	25	2	352	-314	-155
-5	18	2	302	-384	70	0	21	2	165	-268	-97	-3	25	2	677	596	59
-4	18	2	342	-389	-10	1	21	2	118	60	-118	-2	25	2	843	915	54
-3	18	2	1315	-172	29	2	21	2	120	-61	-128	-1	25	2	400	418	74
-2	18	2	247	-237	-120	3	21	2	406	6	-84	0	25	2	1232	1246	33
-1	18	2	242	86	-133	4	21	2	479	-303	75	1	25	2	271	111	-37
0	18	2	169	117	-31	5	21	2	445	-506	-96	2	25	2	667	-717	64
1	18	2	635	553	45	6	21	2	143	-12	-143	3	25	2	467	-350	-79
2	18	2	458	552	61	7	21	2	474	-34	-99	4	25	2	746	-810	63
3	18	2	282	43	-134	-7	22	2	558	-479	87	-5	25	2	851	-740	54
4	18	2	122	130	-122	-6	22	2	782	672	60	6	25	2	156	-77	-156

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	
3 18	2	492	-519	76	-5 22	2	374	-562	113	-6 26	2	536	-539	-95	-4 30	2	389	-355	-140
3 18	2	207	-436	-207	-4 22	2	459	78	-11	-5 26	2	104	-116	48	-4 31	2	145	-35	-45
3 18	2	545	-314	74	-2 22	2	127	-116	34	-3 26	2	1020	101	4	-3 31	2	144	-39	-44
3 18	2	149	-173	-149	-2 22	2	1024	105	40	-3 26	2	115	-152	-2	-2 31	2	152	-21	-152
-8 19	2	337	-333	-185	-1 22	2	321	-17	-17	-1 26	2	408	-125	41	-1 31	2	616	-54	72
-7 19	2	641	569	75	0 22	2	315	-270	124	-2 26	2	408	-142	-102	-1 31	2	238	-65	-118
-6 19	2	466	-376	-90	1 22	2	1438	-104	29	0 26	2	114	-114	46	1 31	2	424	-104	-104
-5 19	2	883	-787	45	1 22	2	236	-248	-236	1 26	2	227	-99	-227	2 31	2	151	-6	-151
-4 19	2	123	115	37	3 22	2	128	-122	18	3 26	2	610	-166	34	3 31	2	442	-26	-106
-3 19	2	570	-100	61	4 22	2	44	-660	54	4 26	2	740	-745	70	4 31	2	378	20	-142
-2 19	2	107	86	-107	5 22	2	805	-798	54	5 26	2	148	-44	81	5 31	2	378	13	-137
-1 19	2	174	174	-25	6 22	2	365	-374	-17	6 26	2	144	-31	-144	-2 32	2	555	-106	90
0 19	2	1040	-1022	21	7 22	2	288	-31	-288	7 26	2	135	892	-61	-2 32	2	555	-106	90
1 19	2	117	156	-117	-7 22	2	218	-397	-18	-6 26	2	136	350	-156	0 32	2	473	345	-91
2 19	2	1153	1184	30	-6 22	2	737	596	51	-5 26	2	331	-217	-170	1 32	2	503	-362	-94
3 19	2	492	-519	76	-5 22	2	374	-562	113	-6 26	2	536	-539	-95	-4 30	2	389	-355	-140
3 18	2	207	-436	-207	-4 22	2	459	78	-11	-5 26	2	104	-116	48	-4 31	2	145	-35	-45
3 18	2	545	-314	74	-2 22	2	127	-116	34	-3 26	2	1020	101	4	-3 31	2	144	-39	-44
3 18	2	149	-173	-149	-2 22	2	1024	105	40	-3 26	2	115	-152	-2	-2 31	2	152	-21	-152
-8 19	2	337	-333	-185	-1 22	2	321	-17	-17	-1 26	2	408	-125	41	-1 31	2	616	-54	72
-7 19	2	641	569	75	0 22	2	315	-270	124	-2 26	2	408	-142	-102	-1 31	2	238	-65	-118
-6 19	2	466	-376	-90	1 22	2	1438	-104	29	0 26	2	114	-114	46	1 31	2	424	-104	-104
-5 19	2	883	-787	45	1 22	2	236	-248	-236	1 26	2	227	-99	-227	2 31	2	151	-6	-151
-4 19	2	123	115	37	3 22	2	128	-122	18	3 26	2	610	-166	34	3 31	2	442	-26	-106
-3 19	2	570	-100	61	4 22	2	44	-660	54	4 26	2	740	-745	70	4 31	2	378	20	-142
-2 19	2	107	86	-107	5 22	2	805	-798	54	5 26	2	148	-44	81	5 31	2	378	13	-137
-1 19	2	174	174	-25	6 22	2	365	-374	-17	6 26	2	144	-31	-144	-2 32	2	555	-106	90
0 19	2	1040	-1022	21	7 22	2	288	-31	-288	7 26	2	135	892	-61	-2 32	2	555	-106	90
1 19	2	117	156	-117	-7 22	2	218	-397	-18	-6 26	2	136	350	-156	0 32	2	473	345	-91
2 19	2	1153	1184	30	-6 22	2	737	596	51	-5 26	2	331	-217	-170	1 32	2	503	-362	-94
3 19	2	492	-519	76	-5 22	2	374	-562	113	-6 26	2	536	-539	-95	-4 30	2	389	-355	-140
3 18	2	207	-436	-207	-4 22	2	459	78	-11	-5 26	2	104	-116	48	-4 31	2	145	-35	-45
3 18	2	545	-314	74	-2 22	2	127	-116	34	-3 26	2	1020	101	4	-3 31	2	144	-39	-44
3 18	2	149	-173	-149	-2 22	2	1024	105	40	-3 26	2	115	-152	-2	-2 31	2	152	-21	-152
-8 19	2	337	-333	-185	-1 22	2	321	-17	-17	-1 26	2	408	-125	41	-1 31	2	616	-54	72
-7 19	2	641	569	75	0 22	2	315	-270	124	-2 26	2	408	-142	-102	-1 31	2	238	-65	-118
-6 19	2	466	-376	-90	1 22	2	1438	-104	29	0 26	2	114	-114	46	1 31	2	424	-104	-104
-5 19	2	883	-787	45	1 22	2	236	-248	-236	1 26	2	227	-99	-227	2 31	2	151	-6	-151
-4 19	2	123	115	37	3 22	2	128	-122	18	3 26	2	610	-166	34	3 31	2	442	-26	-106
-3 19	2	570	-100	61	4 22	2	44	-660	54	4 26	2	740	-745	70	4 31	2	378	20	-142
-2 19	2	107	86	-107	5 22	2	805	-798	54	5 26	2	148	-44	81	5 31	2	378	13	-137
-1 19	2	174	174	-25	6 22	2	365	-374	-17	6 26	2	144	-31	-144	-2 32	2	555	-106	90
0 19	2	1040	-1022	21	7 22	2	288	-31	-288	7 26	2	135	892	-61	-2 32	2	555	-106	90
1 19	2	117	156	-117	-7 22	2	218	-397	-18	-6 26	2	136	350	-156	0 32	2	473	345	-91
2 19	2	1153	1184	30	-6 22	2	737	596	51	-5 26	2	331	-217	-170	1 32	2	503	-362	-94
3 19	2	492	-519	76	-5 22	2	374	-562	113	-6 26	2	536	-539	-95	-4 30	2	389	-355	-140
3 18	2	207	-436	-207	-4 22	2	459	78	-11	-5 26	2	104	-116	48	-4 31	2	145	-35	-45
3 18	2	545	-314	74	-2 22	2	127	-116	34	-3 26	2	1020	101	4	-3 31	2	144	-39	-44
3 18	2	149	-173	-149	-2 22	2	1024	105	40	-3 26	2	115	-152	-2	-2 31	2	152	-21	-152
-8 19	2	337	-333	-185	-1 22	2	321	-17	-17	-1 26	2	408	-125	41	-1 31	2	616	-54	72
-7 19	2	641	569	75	0 22	2	315	-270	124	-2 26	2	408	-142	-102	-1 31	2	238	-65	-118
-6 19	2	466	-376	-90	1 22	2	1438	-104	29	0 26	2	114	-114	46	1 31	2	424	-104	-104
-5 19	2	883	-787	45	1 22	2	236	-248	-236	1 26	2	227	-99	-227	2 31	2	151	-6	-151
-4 19	2	123	115	37	3 22	2	128	-122	18	3 26	2	610	-166	34	3 31	2	442	-26	-106
-3 19	2	570	-100	61	4 22	2	44	-660	54	4 26	2	740	-745	70	4 31	2	378	20	-142
-2 19	2	107	86	-107	5 22	2	805	-798	54	5 26	2	148	-44	81	5 31	2	378	13	-137
-1 19	2	174	174	-25	6 22	2	365	-374	-17	6 26	2	144	-31	-144	-2 32	2	555	-106	90
0 19	2	1040	-1022	21	7 22	2	288	-31	-288	7 26	2	135	892	-61	-2 32	2	555	-106	90
1 19	2	117	156	-117	-7 22	2	218	-397	-18	-6 26	2	136	350	-156	0 32	2	473	345	-91
2 19	2	1153	1184	30	-6 22	2	737	596	51	-5 26	2	331	-217	-170	1 32	2	503	-362	-94
3 19	2	492	-519	76	-5 22	2	374	-562	113	-6 26	2	536	-539	-95	-4 30	2	389	-355	-140
3 18	2	207	-436	-207	-4 22	2	459	78	-11	-5 26	2	104	-116	48	-4 31	2	145	-35	-45
3 18	2	545	-314	74	-2 22	2	127	-116	34	-3 26	2	1020	101	4	-3 31	2	144	-39	-44
3 18	2	149	-173	-149	-2 22	2	1024	105	40	-3 26	2	115	-152	-2	-2 31	2	152	-21	-152
-8 19	2	337	-333	-185	-1 22	2	321	-17	-17	-1 26	2	408	-125	41	-1 31	2	616	-54	72
-7 19	2	641	569	75	0 22	2	315	-270	124	-2 26	2	408	-142	-102	-1 31	2	238	-65	-118
-6 19	2	466	-376	-90	1 22	2	1438	-104	29	0 26	2	114	-114	46	1 31	2	424	-104	-104
-5 19	2	883	-787	45	1 22	2	236	-248	-236	1 26	2	227	-99	-227	2 31	2	151	-6	-151
-4 19	2	123	115	37	3 22	2	128	-122	18	3 26	2	610	-166	34	3 31	2	442	-26	-106
-3 19	2	570	-100	61	4 22	2	44	-660	54	4 26	2	740	-745	70	4 31	2	378	20	-142
-2 19	2	107	86	-107	5 22	2	805	-798	54	5 26	2	148	-44	81	5 31	2	378	13	-137
-1 19	2	174	174	-25	6 22	2	365	-374	-17	6 26	2	144	-31	-144	-2 32	2	555	-106	90
0 19	2	1040	-1022	21	7 22	2	288	-31	-288	7 26	2	135	892	-61	-2 32	2	555	-106	90
1 19	2	117	156	-117	-7 22	2	218	-397	-18	-6 26	2	136	350	-156	0 32	2	473	345	-91
2 19	2	1153	1184	30	-6 22	2	737	596	51	-5 26	2	331	-217	-170	1 32	2	503	-362	-94
3 19	2	492	-519	76	-5 22	2	374	-562	113	-6 26	2	536	-539	-95	-4 30	2	389	-355	-140
3 18	2	207	-436	-207	-4 22	2	459	78	-11	-5 26	2								

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2																												
	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S										
-4	18	3	1220-1307	27	2	7	3	2277	2201	18	1	10	3	866	-752	34	0	13	3	374	320	35	2	16	3	108	134-108	
-3	18	3	999-478	-16	3	7	3	2657	2559	19	2	10	3	306	-65	58	1	13	3	237	176	-97	3	16	3	157	131-157	
-2	18	3	986-969	40	4	7	3	1195	1173	24	3	10	3	592	607	35	2	13	3	372	508	51	4	16	3	495	1457-29	
-1	18	3	458-576	-31	5	7	3	1057	-1043	29	4	10	3	1324	1345	26	3	13	3	503	-604	51	5	16	3	525	374	69
0	18	3	717-623	66	6	7	3	1071	-1008	35	5	10	3	750	811	42	4	13	3	432	420	67	6	16	3	372	112-117	
1	18	3	297-1304	-297	7	7	3	771	-740	50	6	10	3	698	668	50	5	13	3	452	429	68	7	16	3	448	515-104	
2	18	3	1267-1304	45	8	7	3	81-812	-812	54	7	10	3	262	322-262	62	6	13	3	130	-160	-130	8	16	3	14	-181-14	
3	18	3	408-183	-97	9	7	3	438	-778	126	8	10	3	505	-584	92	7	13	3	370	100	-124	8	17	3	948	836	54
4	18	3	550-597	70	10	7	3	262	-420	222	9	10	3	295	-300	246	8	13	3	355	-60	-142	7	17	3	542	347	76
5	18	3	111-1103	34	11	7	3	592	-592	66	9	11	3	948	-784	58	9	13	3	315	43	-196	6	17	3	435	-335	-103
6	18	3	1844-1803	26	12	7	3	153	-160	138	10	11	3	141	-88	141	10	14	3	458	271	-123	5	17	3	129	-228	-39
7	18	3	565-524	41	13	7	3	2092	-1882	25	11	11	3	936	-836	41	11	14	3	146	128	-146	4	17	3	1305	-1342	33
8	18	3	575-490	28	14	7	3	1052	-1014	26	12	11	3	1564	-1552	29	12	14	3	741	-721	62	3	17	3	1790	-1842	26
9	18	3	2827-2834	17	15	7	3	180	-158	26	13	11	3	105	-201	-63	13	14	3	626	507	63	2	17	3	159	-77	-109
10	18	3	766-762	18	16	7	3	894	-477	31	14	11	3	104	-41	-164	14	14	3	896	-648	42	3	17	3	1384	1345	17
11	18	3	1948-1980	60	17	7	3	3080	-3083	19	15	11	3	355	-201	-103	15	14	3	749	-739	41	0	17	3	1667	-1672	25
12	18	3	367-375	35	18	7	3	3080	-3083	19	16	11	3	12421	-2513	20	16	14	3	1953	1881	23	2	17	3	2503	2350	24
13	18	3	4296-4132	18	19	7	3	1258	-132	18	17	11	3	1311	1230	19	17	14	3	1036	-1030	26	2	17	3	243	-9	-32
14	18	3	1078-1030	20	20	7	3	1258	-132	18	18	11	3	351	-272	32	18	14	3	419	-473	50	3	17	3	1335	1348	29
15	18	3	314-305	-72	21	7	3	2777	-2639	21	19	11	3	1058	-1034	21	19	14	3	2077	2037	43	4	17	3	566	536	60
16	18	3	1462-1457	25	22	7	3	176	-474	47	21	11	3	2705	-2749	20	21	14	3	1367	-1413	24	5	17	3	193	-530	-106
17	18	3	1410-1548	29	23	7	3	176	-474	47	22	11	3	1090	-1077	25	22	14	3	540	550	43	6	17	3	737	-87	-13
18	18	3	977-1012	40	24	7	3	1283	-1261	28	24	11	3	107	-211	-107	24	14	3	756	740	35	7	17	3	700	-519	67
19	18	3	212-121-212		25	7	3	1389	-1361	28	25	11	3	958	-889	32	25	14	3	1884	-1804	27	8	17	3	630	-63	81
-19	6	3	777-806	59	26	7	3	1389	-1600	30	26	11	3	1177	-1117	34	26	14	3	311	228	-121	9	18	3	537	-558	26
-18	6	3	475-220	-107	27	7	3	546	-490	47	27	11	3	415	-514	-102	27	14	3	373	394	-112	10	18	3	123	530	30
-17	19	3	475-220	-107	28	8	3	140	-135	135	28	11	3	140	-180	-140	28	14	3	1041	-946	48	11	18	3	388	-793	48
-16	19	3	335-104	-135	29	8	3	496	-202	-95	29	11	3	659	-581	76	29	14	3	475	473	-95	12	18	3	1308	-793	48

-6 19	3 227	183-227	2 22	3 302	-490-225	2 26	3 581	494 75	-3 32	3 464	447-104	-6 2	4 514	-625	62
-3 19	3 392	-264 31	3 22	3 124	100-124	3 26	3 135	-134-135	-2 32	3 555	224 91	-6 2	4 716	-763	35
-4 19	3 1590	1564 31	3 22	3 134	-114 39	3 26	3 134	-114-134	-2 32	3 582	544 67	-6 2	4 1623	1630 20	18
-3 19	3 1034	1039 36	3 22	3 551	-621 82	3 26	3 148	-21-154	0 32	3 103	160 35	-6 2	4 2048	2031 18	18
-2 19	3 119	118-119	6 22	3 145	-142-145	6 26	3 157	86-154	0 32	3 249	-25-149	-1 2	4 2248	2230 17	14
-1 19	3 1226	1251 32	7 22	3 250	-449-258	-5 27	3 302	-40-97	2 32	3 371	80-211	0 2	4 2098	-2026 36	36
0 19	3 969	-944 34	-7 22	3 151	-378-151	-5 27	3 323	418-99	-2 32	3 372	218-212	0 2	4 417	-378 26	26
1 19	3 1965	-1961 30	6 23	3 280	189-280	-3 27	3 144	-80-144	-2 32	3 445	278-108	2 2	4 1143	-1075 17	17
2 19	3 396	-3965 -69	-5 23	3 137	342-137	-3 27	3 496	-411 88	-1 32	3 381	-369-105	2 2	4 3255	-3099 20	20
3 19	3 1396	-1374 30	3 23	3 236	335-236	-1 27	3 111	339-122	0 32	3 400	504 81	4 2	4 1088	-1104 23	23
4 19	3 682	-621 55	-3 23	3 613	826 63	-1 27	3 280	-388-16	2 32	3 478	-396-112	5 2	4 148	-1140 74	74
5 19	3 778	778 54	-2 23	3 1165	1162 37	0 27	3 577	225 16	2 32	3 438	112-112	6 2	4 377	438 78	78
6 19	3 522	279 82	-1 23	3 309	353-125	1 27	3 552	566 71	-10 0	4 807	791 50	7 2	4 1373	1405 34	34
7 19	3 585	615 85	0 23	3 535	-498 43	2 27	3 604	-462 75	-8 0	4 206	-4-206	8 2	4 531	745 82	82
8 19	3 637	716 81	1 23	3 787	-811 44	3 27	3 133	217-554	-7 0	4 2178	2118 28	9 2	4 140	289-140	140
-8 20	3 157	-1595-157	7 23	3 754	-632 53	4 27	3 333	317-554	-5 0	4 1459	1442 26	-10 3	4 892	-930 62	62
-7 20	3 846	685 57	2 23	3 326	-431-123	-5 27	3 446	-581-20	-6 0	4 2434	-203 22	-9 3	4 143	370-143	143
-6 20	3 931	921 51	4 23	3 510	-400 17	-5 28	3 507	353 50	-4 0	4 358	324 50	-8 3	4 134	98-134	134
-5 20	3 698	696 54	5 23	3 266	39-266	-4 28	3 362	280-132	-3 0	4 1935	-317 17	-7 3	4 640	-612 61	61
-4 20	3 881	856 46	6 23	3 394	344-130	-2 28	3 657	235 53	-2 0	4 2243	2164 30	-6 3	4 2243	2164 30	30
-3 20	3 917	-953 39	7 23	3 519	451-250	-2 28	3 500	734 53	-1 0	4 160	65 68	-5 3	4 526	547 46	46
-2 20	3 1316	-1339 32	-7 24	3 302	-280-199	-1 28	3 950	160 53	-1 0	4 2104	-2048 9	-4 3	4 409	394 48	48
-1 20	3 301	-62-100	-6 24	3 534	581 78	1 28	3 958	47 53	1 0	4 333	-308 32	-3 3	4 2221	-2210 16	16
0 20	3 1354	-1308 24	-5 24	3 800	786 55	2 28	3 713	177-773	3 0	4 6470	6412 17	-2 2	4 2991	-3045 15	15
1 20	3 1075	-1114 37	-4 24	3 321	-519-122	2 28	3 788	780 40	3 0	4 623	627 28	-1 3	4 951	907 21	21
2 20	3 219	144-219	-3 24	3 702	671 34	4 28	3 363	241-184	4 0	4 91	-51 31	0 3	4 2001	-1956 15	15
3 20	3 651	744 55	-2 24	3 452	-282 -44	5 28	3 288	217-184	5 0	4 1563	1587 24	1 3	4 590	-613 24	24
4 20	3 1119	1063 39	0 24	3 1205	-1273 35	-5 28	3 146	326 146	6 0	4 147	-438 25	2 3	4 1559	1012 22	22
5 20	3 847	933 50	0 24	3 226	152-04	-5 29	3 146	326 146	7 0	4 123	-213-123	3 3	4 1106	-1179 23	23
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-8 21	3 304	162-842	2 24	3 710	-656 55	-3 29	3 142	161-45	9 0	4 1125	-1129 44	5 3	4 1254	1273 31	31
-7 21	3 469	509-97	4 24	3 1040	1079 43	-2 29	3 142	161-45	-10 0	4 1366	1133-146	6 3	4 591	-582 -97	97
-6 21	3 946	881 51	5 24	3 304	374-202	0 29	3 236	326 121	-9 1	4 1087	1089 47	7 3	4 243	389-243	243
-5 21	3 187	-1389 37	6 24	3 659	612 80	1 29	3 110	-780 141	-8 1	4 459	316 76	8 3	4 386	-40-128	128
-4 21	3 312	-380-146	-6 25	3 382	-348-140	2 29	3 143	-780 141	-7 1	4 1251	-1215 35	9 3	4 232	24-232	24
-3 21	3 606	-883 59	-5 25	3 236	300-236	3 29	3 457	-612-109	-6 1	4 124	-3142-124	-10 4	4 317	-80-176	176
-2 21	3 2054	-2046 28	-4 25	3 716	-664 59	4 29	3 406	-304-102	-5 1	4 2403	-2417 23	-9 4	4 1107	1115 44	44
-1 21	3 549	599 53	-3 25	3 700	-599 54	5 29	3 518	308 193	-4 1	4 5822	-5663 20	-8 4	4 310	333-132	132
0 21	3 388	604 93	-2 25	3 797	823 53	-4 30	3 361	602-182	-3 1	4 1166	1185 18	-7 4	4 310	333-132	132
1 21	3 108	-251-118	-1 25	3 599	-604 63	-3 30	3 150	-610-150	-2 1	4 655	-687 20	-6 4	4 116	-55-116	116

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S
-5 4	4	1291	1320 28	-8 7	4	139	-119-139	-9 10	4	871	776 61	-7 16	4	907	-934 55
-4 4	4	1961	-2043 20	-7 7	4	595	583 69	-8 10	4	204	-82-204	-6 16	4	670	-703 66

1338	1119	20	-5	7	4	1151	-1098	37	-7	10	4	4231	1154	41	-8	3	154	-327	-154	-5	16	4	809	806	68	
212	44	-61	-5	7	4	108	71	-108	-5	10	4	108	71	-108	-5	10	4	108	71	-108	-5	10	4	108	71	-108
2880	-238	16	-3	7	4	200	208	-88	-3	7	4	200	208	-88	-3	7	4	200	208	-88	-3	7	4	200	208	-88
1039	1057	15	-2	7	4	121	1058	37	-2	7	4	121	1058	37	-2	7	4	121	1058	37	-2	7	4	121	1058	37
1376	1375	15	-2	7	4	86	666	56	-2	7	4	86	666	56	-2	7	4	86	666	56	-2	7	4	86	666	56
409	-401	35	-1	7	4	129	179	11	-1	7	4	129	179	11	-1	7	4	129	179	11	-1	7	4	129	179	11
2406	2355	15	-1	7	4	196	145	16	-1	7	4	196	145	16	-1	7	4	196	145	16	-1	7	4	196	145	16
1301	-1272	28	7	7	4	115	1064	10	7	10	4	115	1064	10	7	10	4	115	1064	10	7	10	4	115	1064	10
361	688	50	7	7	4	810	768	27	7	10	4	810	768	27	7	10	4	810	768	27	7	10	4	810	768	27
590	508	70	7	7	4	713	657	32	7	10	4	713	657	32	7	10	4	713	657	32	7	10	4	713	657	32
707	670	61	7	7	4	713	657	32	7	10	4	713	657	32	7	10	4	713	657	32	7	10	4	713	657	32
141	139	-41	7	7	4	221	213	21	7	10	4	221	213	21	7	10	4	221	213	21	7	10	4	221	213	21
151	138	-53	7	7	4	374	395	12	7	10	4	374	395	12	7	10	4	374	395	12	7	10	4	374	395	12
145	238	-45	7	7	4	695	638	64	7	10	4	695	638	64	7	10	4	695	638	64	7	10	4	695	638	64
139	183	-139	9	7	4	313	197	150	9	7	4	313	197	150	9	7	4	313	197	150	9	7	4	313	197	150
283	66	-171	7	7	4	317	157	124	7	10	4	317	157	124	7	10	4	317	157	124	7	10	4	317	157	124
979	-1009	30	-8	8	4	393	312	56	-8	8	4	393	312	56	-8	8	4	393	312	56	-8	8	4	393	312	56
1012	-946	29	-7	8	4	410	143	106	-7	8	4	410	143	106	-7	8	4	410	143	106	-7	8	4	410	143	106
188	516	26	-6	8	4	319	42	11	-6	8	4	319	42	11	-6	8	4	319	42	11	-6	8	4	319	42	11
257	1042	18	-5	8	4	114	186	14	-5	8	4	114	186	14	-5	8	4	114	186	14	-5	8	4	114	186	14
1007	-1042	18	-5	8	4	710	350	32	-5	8	4	710	350	32	-5	8	4	710	350	32	-5	8	4	710	350	32
205	2257	15	-3	8	4	259	70	70	-3	8	4	259	70	70	-3	8	4	259	70	70	-3	8	4	259	70	70
527	788	31	-2	8	4	1201	1209	17	-2	8	4	1201	1209	17	-2	8	4	1201	1209	17	-2	8	4	1201	1209	17
1003	938	19	-1	8	4	1352	1351	20	-1	8	4	1352	1351	20	-1	8	4	1352	1351	20	-1	8	4	1352	1351	20
850	-813	28	2	8	4	500	509	14	2	8	4	500	509	14	2	8	4	500	509	14	2	8	4	500	509	14
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370	777	51	-7	8	4	315	125	127	-7	8	4	315	125	127	-7	8	4	315	125	127	-7	8	4	315	125	127
430	436	87	7	8	4	315	611	107	7	8	4	315	611	107	7	8	4	315	611	107	7	8	4	315	611	107
158	101	26	-6	8	4	264	35	173	-6	8	4	264	35	173	-6	8	4	264	35	173	-6	8	4	264	35	173
158	101	26	-6	8	4	1571	1509	28	-6	8	4	1571	1509	28	-6	8	4	1571	1509	28	-6	8	4	1571	1509	28
158	101	26	-6	8	4	886	958	27	-6	8	4	886	958	27	-6	8	4	886	958	27	-6	8	4	886	958	27
158	101	26	-6	8	4	1255	1215	23	-6	8	4	1255	1215	23	-6	8	4	1255	1215	23	-6	8	4	1255	1215	23
158	101	26	-6	8	4	901	913	20	-6	8	4	901	913	20	-6	8	4	901	913	20	-6	8	4	901	913	20
158	101	26	-6	8	4	1957	2071	58	-6	8	4	1957	2071	58	-6	8	4	1957	2071	58	-6	8	4	1957	2071	58
158	101	26	-6	8	4	731	768	24	-6	8	4	731	768	24	-6	8	4	731	768	24	-6	8	4	731	768	24
158	101	26	-6	8	4	1035	1038	21	-6	8	4	1035	1038	21	-6	8	4	1035	1038	21	-6	8	4	1035	1038	21
431	439	62	4	8	4	230	235	24	4	8	4	230	235	24	4	8	4	230	235	24	4	8	4	230	235	24

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2																															
H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S								
5	6	4	611	725	52	5	9	4	114	62-114	4	12	4	1133	-1163	30	5	15	4	1088	-1075	36	-7	19	4	563	464	80			
6	6	4	430	-439	-91	6	9	4	354	295-101	5	12	4	662	571	45	6	15	4	559	-505	54	-4	19	4	996	-960	48			
7	6	4	134	23	-134	7	9	4	687	837	65	6	12	4	227	-72	27	7	15	4	559	-505	74	-5	19	4	130	57	130		
8	6	4	462	420	-105	8	9	4	374	-411-130	7	12	4	965	1085	48	8	15	4	574	23	-144	-4	19	4	538	41	65			
9	7	4	239	-338	-239	9	9	4	338	-114-166	8	12	4	804	873	53	-8	16	4	512	231	-135	-3	19	4	869	-804	38			
2	19	4	759	698	41	7	22	4	645	394	73	-6	7	4	558	389	84	-2	23	4	681	-443	74	2	3	5	331	287	45		
1	19	4	385	-20	-71	-7	23	4	215	-167-215	-5	7	4	830	897	53	-1	33	4	550	-519	-174	3	3	5	1353	1278	19			
0	19	4	567	-616	49	-6	23	4	935	888	51	-4	7	4	328	528	71	0	33	4	707	321	67	4	3	5	1694	1703	22		
1	19	4	130	1764	26	-5	23	4	467	187	90	-2	7	4	398	-245	-106	1	33	4	200	-480	-20	5	3	5	117	432	-117		
2	19	4	302	-239	-91	-4	23	4	136	-37	-136	-2	7	4	242	387	-42	-10	1	33	5	134	-380	-90	6	3	5	357	359	-92	
3	19	4	764	-759	45	-3	23	4	1114	1211	37	-1	7	4	671	-626	61	-9	1	33	5	135	-345	-16	7	3	5	207	-388	-207	
4	19	4	131	440	-131	-2	23	4	1146	-1045	37	0	7	4	299	-1168	38	-9	1	33	5	138	-445	52	8	3	5	696	-668	58	
5	19	4	611	-614	65	-1	23	4	311	-403	-120	1	7	4	299	-493	-175	-7	1	33	5	234	-358	-234	-10	4	3	310	-345	-171	
6	19	4	217	-104	-127	0	23	4	121	-110	-86	2	7	4	760	-693	65	-6	1	33	5	232	-122	2	-10	4	3	234	213	-234	
7	19	4	430	433	-110	1	23	4	1441	-1460	32	3	7	4	144	337	-44	-5	1	33	5	214	293	46	-8	4	3	1034	1027	53	
8	20	4	512	-511	-101	2	23	4	404	333	-106	4	27	4	881	921	62	-4	1	33	5	214	293	46	-7	4	3	132	94	-132	
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6	20	4	142	200	-142	4	23	4	468	-432	-89	-5	28	4	406	253	-123	-2	1	33	5	353	-859	17	-5	4	3	264	-265	24	
5	20	4	801	-794	48	5	23	4	1061	1010	44	-4	28	4	672	-616	67	-1	1	33	5	340	323	16	-4	4	3	1584	-1708	21	
4	20	4	970	988	43	6	23	4	501	558	-96	-3	28	4	780	-793	58	1	1	33	5	57	-657	19	-3	4	3	83	-75	-83	
3	20	4	259	-86	-153	7	23	4	152	-15	-152	-2	28	4	590	-475	73	1	1	33	5	558	553	29	-2	4	3	1375	-1396	16	
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1	20	4	157	1462	38	-6	24	4	390	263	-134	1	28	4	439	519	-53	5	1	33	5	137	-211	-127	0	4	3	5	1826	-1617	41
0	20	4	362	-307	-70	-5	24	4	428	398	-102	2	28	4	407	488	77	5	1	33	5	137	-211	-127	0	4	3	5	366	-447	36
1	20	4	660	-648	50	-4	24	4	756	-695	56	2	28	4	655	777	71	7	1	33	5	520	554	67	2	4	3	3427	3254	20	
2	20	4	161	1120	37	-3	24	4	976	-869	44	4	28	4	419	308	-114	7	1	33	5	520	554	67	2	4	3	5	1000	974	22
3	20	4	469	-423	70	-2	24	4	677	-684	60	4	28	4	324	-191	131	9	1	33	5	520	554	67	2	4	3	2436	-278	21	
4	20	4	127	33	-127	1	24	4	782	-741	48	5	28	4	131	-113	131	9	1	33	5	520	554	67	2	4	3	5	426	-354	67
5	20	4	687	759	62	0	24	4	530	406	46	-5	28	4	146	-152	-146	-10	2	33	5	520	554	67	2	4	3	5	1428	1567	30
6	20	4	742	-187	64	1	24	4	442	671	-100	-7	29	4	146	-152	-146	-10	2	33	5	520	554	67	2	4	3	5	426	-354	67
7	20	4	422	193	-113	2	24	4	215	362	-215	-3	29	4	1061	-963	47	-10	2	33	5	520	554	67	2	4	3	5	964	-910	45
8	21	4	451	35	-107	3	24	4	883	985	51	-2	29	4	669	753	73	-7	2	33	5	520	554	67	2	4	3	5	492	428	79
7	21	4	393	-36	-132	4	24	4	685	713	64	1	29	4	693	810	68	-7	2	33	5	520	554	67	2	4	3	5	142	-219	-142
6	21	4	143	-97	-172	5	24	4	143	49	-143	0	29	4	136	-29	-96	-6	2	33	5	520	554	67	2	4	3	5	505	-224	-102
5	21	4	294	-278	-172	6	24	4	150	-12	-150	1	29	4	112	198	43	-6	2	33	5	520	554	67	2	4	3	5	396	-369	-35
4	21	4	534	570	57	-6	25	4	150	-158	-150	2	29	4	144	-342	-144	-4	2	33	5	520	554	67	2	4	3	5	313	240	-188
3	21	4	578	-464	58	-5	25	4	1091	-1073	43	4	29	4	146	-342	-144	-4	2	33	5	520	554	67	2	4	3	5	2015	-1529	33
2	21	4	474	-420	61	-3	25	4	132	-30	-132	-4	30	4	566	306	91	-2	2	33	5	520	554	67	2	4	3	5	613	-615	48
1	21	4	751	722	32	-2	25	4	205	-89	-205	-3	30	4	432	439	-115	0	2	33	5	520	554	67	2	4	3	5	281	-52	85
0	21	4	357	284	-91	-1	25	4	980	1036	41	-2	30	4	333	438	-115	0	2	33	5	520	554	67	2	4	3	5	1310	-1253	20
1	21	4	150	-143	-130	0	25	4	1037	1069	37	-1	30	4	955	962	52	-2	2	33	5	520	554	67	2	4	3	5	2576	2581	20
2	21	4	575	532	60	1	25	4	556	300	63	0	30	4	584	-561	52	2	2	33	5	520	554	67	2	4	3	5	1778	1718	17

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S
-1	22	5	890	848	38	0	26	5	129	15	-91	-2	22	5	440	-386	126
0	22	5	1185	1216	26	1	26	5	628	492	38	-1	32	5	259	406	229
1	22	5	124	-10	-124	2	26	5	233	16	-233	0	32	5	229	330	50
2	22	5	1471	1495	35	3	26	5	281	146	-235	1	32	5	342	227	105
3	22	5	513	627	70	4	26	5	170	-207	1	2	32	5	368	471	-157
4	22	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
5	22	5	336	-256	-138	-6	27	5	282	47	-282	0	33	5	144	18	-156
6	22	5	707	-835	75	-7	27	5	358	444	-159	1	33	5	184	37	132
7	22	5	609	-580	78	-8	27	5	489	-371	-93	2	33	5	134	177	-134
-7	23	5	132	-270	-132	-9	0	6	135	-40	105	3	33	5	266	359	-84
-6	23	5	655	-604	71	-2	27	5	145	-110	-145	4	33	5	291	105	105
-5	23	5	890	848	38	0	26	5	129	15	-91	-2	22	5	440	-386	126
-4	23	5	1185	1216	26	1	26	5	628	492	38	-1	32	5	259	406	229
-3	23	5	124	-10	-124	2	26	5	233	16	-233	0	32	5	229	330	50
-2	23	5	1471	1495	35	3	26	5	281	146	-235	1	32	5	342	227	105
-1	23	5	513	627	70	4	26	5	170	-207	1	2	32	5	368	471	-157
0	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
1	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
2	23	5	336	-256	-138	-6	27	5	282	47	-282	0	33	5	144	18	-156
3	23	5	707	-835	75	-7	27	5	358	444	-159	1	33	5	184	37	132
4	23	5	609	-580	78	-8	27	5	489	-371	-93	2	33	5	134	177	-134
5	23	5	132	-270	-132	-9	0	6	135	-40	105	3	33	5	266	359	-84
6	23	5	655	-604	71	-2	27	5	145	-110	-145	4	33	5	291	105	105
7	23	5	890	848	38	0	26	5	129	15	-91	-2	22	5	440	-386	126
8	23	5	1185	1216	26	1	26	5	628	492	38	-1	32	5	259	406	229
9	23	5	124	-10	-124	2	26	5	233	16	-233	0	32	5	229	330	50
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11	23	5	513	627	70	4	26	5	170	-207	1	2	32	5	368	471	-157
12	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
13	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
14	23	5	336	-256	-138	-6	27	5	282	47	-282	0	33	5	144	18	-156
15	23	5	707	-835	75	-7	27	5	358	444	-159	1	33	5	184	37	132
16	23	5	609	-580	78	-8	27	5	489	-371	-93	2	33	5	134	177	-134
17	23	5	132	-270	-132	-9	0	6	135	-40	105	3	33	5	266	359	-84
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19	23	5	890	848	38	0	26	5	129	15	-91	-2	22	5	440	-386	126
20	23	5	1185	1216	26	1	26	5	628	492	38	-1	32	5	259	406	229
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23	23	5	513	627	70	4	26	5	170	-207	1	2	32	5	368	471	-157
24	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
25	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
26	23	5	336	-256	-138	-6	27	5	282	47	-282	0	33	5	144	18	-156
27	23	5	707	-835	75	-7	27	5	358	444	-159	1	33	5	184	37	132
28	23	5	609	-580	78	-8	27	5	489	-371	-93	2	33	5	134	177	-134
29	23	5	132	-270	-132	-9	0	6	135	-40	105	3	33	5	266	359	-84
30	23	5	655	-604	71	-2	27	5	145	-110	-145	4	33	5	291	105	105
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32	23	5	1185	1216	26	1	26	5	628	492	38	-1	32	5	259	406	229
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35	23	5	513	627	70	4	26	5	170	-207	1	2	32	5	368	471	-157
36	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
37	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
38	23	5	336	-256	-138	-6	27	5	282	47	-282	0	33	5	144	18	-156
39	23	5	707	-835	75	-7	27	5	358	444	-159	1	33	5	184	37	132
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41	23	5	132	-270	-132	-9	0	6	135	-40	105	3	33	5	266	359	-84
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45	23	5	124	-10	-124	2	26	5	233	16	-233	0	32	5	229	330	50
46	23	5	1471	1495	35	3	26	5	281	146	-235	1	32	5	342	227	105
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48	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
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50	23	5	336	-256	-138	-6	27	5	282	47	-282	0	33	5	144	18	-156
51	23	5	707	-835	75	-7	27	5	358	444	-159	1	33	5	184	37	132
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56	23	5	1185	1216	26	1	26	5	628	492	38	-1	32	5	259	406	229
57	23	5	124	-10	-124	2	26	5	233	16	-233	0	32	5	229	330	50
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63	23	5	707	-835	75	-7	27	5	358	444	-159	1	33	5	184	37	132
64	23	5	609	-580	78	-8	27	5	489	-371	-93	2	33	5	134	177	-134
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66	23	5	655	-604	71	-2	27	5	145	-110	-145	4	33	5	291	105	105
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71	23	5	513	627	70	4	26	5	170	-207	1	2	32	5	368	471	-157
72	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
73	23	5	628	-756	71	5	26	5	147	-12	-47	-1	33	5	787	115	66
74	23	5	336	-256	-138	-6	27	5	282	47	-282	0	33	5	144	18	-156

5	23	5	571	-493	74	-1	27	5	646	-693	66	7	0	6	1992	2067	29	9	2	6	341	417	150	6	5	302	-114	123	
4	23	5	135	214	-135	0	27	5	578	547	56	-6	0	6	110	176	-10	-10	3	6	347	423	151	6	5	565	-425	70	
3	23	5	450	659	-87	1	27	5	133	0	-133	10	-9	0	6	1311	1284	25	-9	3	6	501	478	134	6	5	236	-173	-236
2	23	5	890	826	48	2	27	5	223	-161	-223	-4	0	6	2144	2216	20	-7	3	6	1205	1193	38	6	5	230	-18	-230	
1	23	5	559	506	58	3	27	5	314	37	-203	-7	0	6	2584	-2559	19	-6	3	6	345	-125	0	6	5	150	168	150	
0	23	5	256	-119	-112	4	27	5	455	-365	104	-2	0	6	1228	-1250	17	-5	3	6	346	-102	36	6	5	730	173	54	
-1	23	5	458	508	-77	5	27	5	139	-139	-149	-1	0	6	4222	-4303	1	-4	3	6	2688	293	21	6	5	912	906	38	
-2	23	5	141	-151	-141	6	27	5	233	255	-223	0	0	6	2550	-2489	12	-4	3	6	2688	293	21	6	5	652	646	58	
-3	23	5	832	-794	46	-4	28	5	371	-238	-133	2	0	6	2925	2935	15	-4	3	6	2673	1705	20	6	5	6037	-210	40	
-4	23	5	664	-685	65	-3	28	5	666	-854	74	2	0	6	250	-182	-59	-2	3	6	1777	145	16	6	5	1420	416	20	
-5	23	5	146	-455	-146	-2	28	5	654	679	75	2	0	6	268	-328	-72	-1	3	6	1684	-441	33	6	5	6	81	131	-81
-6	23	5	146	35	-146	1	28	5	408	-389	-111	4	0	6	3187	3508	22	0	3	6	2785	2785	18	6	5	1711	-1671	16	
-7	23	5	146	135	-146	0	28	5	136	57	-96	4	0	6	861	799	32	1	3	6	570	-557	31	6	5	2130	2089	37	
-8	23	5	675	705	74	1	28	5	1444	174	40	6	0	6	549	732	56	1	3	6	1703	1718	21	6	5	1711	-1737	17	
-9	23	5	137	-261	-137	2	28	5	514	-402	-95	7	0	6	528	536	56	2	3	6	103	-144	101	6	5	1744	-1737	19	
0	24	5	630	610	65	3	28	5	138	-115	-138	8	0	6	1176	-1263	38	3	3	6	223	296	24	6	5	1041	2000	20	
1	24	5	1050	1087	42	4	28	5	461	371	-116	9	0	6	659	-601	-58	4	3	6	223	296	24	6	5	1361	-1278	24	
2	24	5	1187	-1193	40	-5	28	5	614	-60	87	-10	1	6	521	601	-90	7	3	6	830	717	45	6	5	640	-806	35	
3	24	5	283	171	-142	5	29	5	149	-56	-149	-9	1	6	1087	976	79	8	3	6	891	899	52	6	5	6	709	711	48
4	24	5	339	-309	-76	6	29	5	461	351	-105	-8	1	6	273	376	-170	9	3	6	302	-534	123	6	5	6	601	-819	73
5	24	5	1571	-1497	31	-3	29	5	145	-116	-145	-6	1	6	692	578	50	-10	4	6	702	-534	82	6	5	6	439	459	-111
6	24	5	528	378	74	-2	29	5	604	583	70	-6	1	6	284	286	-105	9	4	6	431	-228	119	6	5	6	339	293	-112
7	24	5	442	-353	-90	-1	29	5	893	86	53	-5	1	6	1880	-1930	23	-9	4	6	312	443	130	6	5	6	497	-486	-160
8	24	5	400	-441	-120	0	29	5	281	-14	-123	-4	1	6	1253	-1319	71	-6	4	6	121	-126	131	6	5	6	590	563	61
9	24	5	1090	1052	49	1	29	5	299	-49	-288	-3	1	6	2122	-2060	18	-7	4	6	660	659	37	6	5	6	933	-926	35
0	24	5	564	-2	-564	2	29	5	818	-82	61	-2	1	6	569	541	72	-5	4	6	407	404	47	6	5	6	165	1655	26
1	24	5	453	341	-119	3	29	5	335	-67	-173	-1	1	6	815	866	15	-4	4	6	746	784	24	6	5	6	909	-914	27
2	24	5	482	525	-91	4	29	5	578	666	-97	3	1	6	1000	1614	15	-3	4	6	431	438	27	6	5	6	1190	-1224	21
3	24	5	788	787	52	3	30	5	337	37	-152	-2	1	6	592	2783	19	-2	4	6	6538	-2631	17	6	5	6	1795	1798	19
4	24	5	275	-121	-195	-2	30	5	577	322	80	-3	1	6	92	184	92	-4	4	6	704	-216	-47	6	5	6	1332	-1201	17
5	24	5	1344	-187	33	1	30	5	572	-263	-140	4	1	6	114	-46	131	-5	4	6	1428	-1308	17	6	5	6	188	179	-80
6	24	5	817	764	33	3	30	5	768	-690	40	4	1	6	109	-50	-105	-6	4	6	86	-2	-86	6	5	6	278	263	19
7	24	5	138	-939	-138	1	30	5	345	-399	-157	5	1	6	1372	-1390	30	-7	4	6	1903	1853	20	6	5	6	2824	-2738	20
8	24	5	142	-34	-142	2	30	5	490	-474	-109	6	1	6	1176	-1174	32	-8	4	6	103	-122	101	6	5	6	681	685	32
9	24	5	1171	1276	44	3	30	5	147	-70	-147	8	1	6	413	-75	-35	-9	4	6	431	438	27	6	5	6	1594	1267	26
0	24	5	395	281	-37	4	30	5	395	281	-37	9	1	6	183	-218	61	-10	4	6	436	436	67	6	5	6	1484	1493	28
1	24	5	143	-176	-143	-3	31	5	661	761	80	-10	2	6	595	542	95	-7	4	6	866	-919	46	6	5	6	593	434	54
2	24	5	13	-13	-13	3	31	5	928	900	58	0	2	6	475	69	-103	0	4	6	136	-65	136	6	5	6	160	16	-190
3	24	5	518	586	-107	4	31	5	661	761	80	0	2	6	317	-388	-159	1	4	6	357	342	139	6	5	6	735	-63	-64
4	24	5	212	-118	-212	0	31	5	621	-633	97	-8	2	6	641	-680	52	2	4	6	640	451	79	6	5	6	327	376	-89
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7	24	5	422	-424	-422	-3	32	5	353	-14	-145	-4	2	6	288	137	-79	-10	4	6	163	135	-163	6	5	6	469	75	-66

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S
-6	8	6	291 -343-130	-6	11	6	619 435 54	-4	4	6	440 390 64	0	17	6	107 78 76
-5	8	6	396-359-67	-5	11	6	1907-190 26	-3	4	6	108 233-106	0	17	6	296 -276-103
-4	8	6	217 250-118	-4	11	6	1111-164 27	-3	4	6	153-169 23	0	17	6	2010-2034 25
-3	8	6	91-148-91	-3	11	6	177-198-77	-1	4	6	282-282 22	0	17	6	117 102-117
-2	8	6	526 496 31	-2	11	6	1912-198 20	0	4	6	98 133-9	0	17	6	45 -97 75
-1	8	6	175 1363 18	-1	11	6	600 508 30	1	4	6	1065-98 25	0	17	6	137 -24 137
0	8	6	81-39-57	0	11	6	870 851 41	1	4	6	165 386 23	0	17	6	1066 184 17
1	8	6	86 81-79	1	11	6	848 786 28	3	4	6	166 358 23	0	17	6	113 588 13
2	8	6	95-67-89	2	11	6	858 764 22	4	4	6	190 145 23	0	17	6	117 163 117
3	8	6	938 380 26	3	11	6	852 880 32	5	4	6	145 123 23	0	17	6	127 371-128
4	8	6	457 364 52	4	11	6	812-807 38	6	4	6	546 502 23	0	17	6	128 135-128
5	8	6	609-621 52	5	11	6	274-341-35	7	4	6	127 -406 63	0	17	6	136 -135-128
6	8	6	328 -282-114	6	11	6	1144-1060 36	8	4	6	150 386 23	0	17	6	136 -135-128
7	8	6	138 50-93	7	11	6	956-965 49	9	4	6	149 379 23	0	17	6	136 -135-128
8	6	6	487 258 93	8	11	6	143 -154 23	10	4	6	150 386 23	0	17	6	136 -135-128
9	8	6	554 221 85	9	12	6	370 18-160 21	11	4	6	150 386 23	0	17	6	136 -135-128
-9	9	6	1665-1082 59	-9	12	6	399 -302-113	-6	13	6	137 401 23	0	17	6	136 -135-128
-8	9	6	295 116-201	-8	12	6	438 -512-100	-5	13	6	184 401 23	0	17	6	136 -135-128
-7	9	6	136 -120-136	-7	12	6	1397-1359 36	-4	13	6	1397-1359 36	0	17	6	136 -135-128
-6	9	6	413 -507-88	-6	12	6	888 -906 39	-3	13	6	183-194 42	0	17	6	136 -135-128
-5	9	6	1783 1822 25	-5	12	6	335 66-78	-2	13	6	569 -351 22	0	17	6	136 -135-128
-4	9	6	393 436 61	-4	12	6	419 351 51	-1	13	6	408 351 22	0	17	6	136 -135-128
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-2	9	6	257 2334 19	-2	12	6	2021 1980 21	1	15	6	180 171 25	0	17	6	136 -135-128
-1	9	6	200-1967 18	-1	12	6	763 712 50	2	15	6	180 171 25	0	17	6	136 -135-128
0	9	6	1636-1446 17	0	12	6	1817 1784 22	3	15	6	418 662 47	0	17	6	136 -135-128
1	9	6	348 350 53	1	12	6	713 -726 34	4	15	6	498 662 47	0	17	6	136 -135-128
2	9	6	1435-1407 21	2	12	6	1582-1563 24	5	15	6	518 -353 41	0	17	6	136 -135-128
3	9	6	335 346 72	3	12	6	854 -897 38	6	15	6	1138-1108 39	0	17	6	136 -135-128
4	9	6	331 356 -86	4	12	6	1288-1356 32	7	15	6	485 -420 37	0	17	6	136 -135-128
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6	9	6	1212 1127 34	6	12	6	339-213-95	9	15	6	14 133-14	0	17	6	136 -135-128
7	9	6	655 560 61	7	12	6	323 197-171	10	15	6	133-133 0	0	17	6	136 -135-128
8	9	6	301 -197-185	8	12	6	339-213-95	11	15	6	165 460 42	0	17	6	136 -135-128
9	9	6	421 346-166	9	13	6	137-125-137	12	15	6	165 460 42	0	17	6	136 -135-128
-9	10	6	158 -189-158	-9	13	6	137-125-137	-5	16	6	1015-1051 30	0	17	6	136 -135-128
-8	10	6	505-302 84	-8	13	6	993 916 44	-3	16	6	182 189 41	0	17	6	136 -135-128
-7	10	6	1715 1698 35	-7	13	6	993 916 44	-2	16	6	182 189 41	0	17	6	136 -135-128
-6	10	6	134 100-124	-6	13	6	2552 2049 26	-1	16	6	132 -133 12	0	17	6	136 -135-128
-5	10	6	435 268 63	-5	13	6	2454 2254 22	0	16	6	305 410 -55	0	17	6	136 -135-128
-4	10	6	1356 1376 26	-4	13	6	257 -96-88	1	16	6	564 411 49	0	17	6	136 -135-128
-3	10	6	2386 2488 21	-3	13	6	1336 1316 22	2	16	6	114 -143-14	0	17	6	136 -135-128
-2	10	6	734 -777 27	-2	13	6	1039-1436 21	3	16	6	408 411 49	0	17	6	136 -135-128
-1	10	6	624 641 29	-1	13	6	2415-2718 22	4	16	6	213-223 28	0	17	6	136 -135-128
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2																													
H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S						
1	10	6	548	500	34	3	13	6	1374	1399	26	6	16	6	142	135	-142	-3	20	6	936	-1073	42	-5	24	6	421	434	-109
2	10	6	1391	1365	22	4	13	6	677	-667	46	7	16	6	245	-300	-115	-1	20	6	535	562	61	-4	24	6	312	-407	-166
3	10	6	617	-624	37	5	13	6	1364	1315	30	8	16	6	840	586	-18	-1	20	6	797	823	40	-3	24	6	130	225	-130
4	10	6	2444	2485	25	6	13	6	137	-447	-137	-8	17	6	309	161	-25	-7	17	6	1343	-1385	23	-2	24	6	667	-654	62
5	10	6	581	605	53	7	13	6	1170	1117	44	-6	17	6	773	-237	-223	-2	20	6	598	700	57	-1	24	6	882	-956	47
6	10	6	667	-777	57	8	13	6	761	812	64	-6	17	6	222	-63	-45	-3	20	6	785	-721	41	-1	24	6	283	-2	-120
7	10	6	546	606	84	9	14	6	443	122	-119	-5	17	6	728	37	-120	-4	20	6	598	570	64	-2	24	6	702	-417	60
8	10	6	594	-534	73	-8	14	6	666	663	72	-4	17	6	420	38	-120	-3	20	6	598	570	64	-2	24	6	134	-5	-134
9	11	6	757	790	76	-7	14	6	139	118	-159	-3	17	6	633	137	64	-8	20	6	137	-127	-137	-3	24	6	1289	1220	36
-8	11	6	449	330	-96	-6	14	6	1640	1430	37	-2	17	6	1135	1168	28	-6	20	6	399	-95	-124	-4	24	6	558	580	33
-7	11	6	436	461	-102	-5	14	6	978	955	38	-1	17	6	1349	-1359	26	-7	20	6	547	472	82	-5	24	6	428	469	-123
6	24	6	400	404	-339	-4	29	6	145	98	-145	-3	2	7	2767	-2680	21	-2	5	7	967	949	23	-2	8	7	93	111	-93
-6	25	6	146	71	-446	-4	30	6	234	400	-234	-4	2	7	966	-522	51	-3	5	7	99	81	-99	-3	8	7	2218	2154	21
-5	25	6	698	-774	70	-3	30	6	420	-246	-113	-5	2	7	923	996	35	-4	5	7	2435	-2466	23	-4	8	7	719	676	36
-4	25	6	757	-608	56	-2	30	6	155	488	-155	-6	2	7	740	-766	45	-5	5	7	340	-352	-88	-5	8	7	877	-865	38
-3	25	6	434	-483	-100	-1	30	6	770	646	57	-7	2	7	7046	1098	41	-6	5	7	594	-580	54	-6	8	7	125	143	-125
-2	25	6	788	-790	54	0	30	6	262	-322	-121	-8	2	7	696	682	63	-7	5	7	866	-893	50	-7	8	7	1148	-1176	42
-1	25	6	333	313	-137	1	30	6	721	574	66	-9	2	7	517	-472	-94	-8	5	7	874	893	51	-8	8	7	787	-869	62
0	25	6	131	169	-93	2	30	6	424	-30	-115	-9	3	7	144	-32	-144	-9	5	7	149	449	-149	-9	9	7	263	201	-263
1	25	6	576	720	75	3	30	6	789	-810	48	-9	3	7	125	-131	-125	-9	5	7	880	-825	56	-9	9	7	202	-31	-202
2	25	6	1842	1725	33	-3	31	6	145	136	-145	-1	3	7	139	101	-95	-8	6	7	241	-240	-241	-7	9	7	1747	-1739	29
3	25	6	534	450	80	-2	31	6	491	87	-105	-5	3	7	158	1528	28	-7	6	7	671	613	46	-5	9	7	548	-516	48
4	25	6	142	-70	-142	-1	31	6	300	-102	-247	-5	3	7	942	856	27	-6	6	7	1124	-117	39	-4	9	7	102	-142	-102
5	25	6	207	-123	-207	0	31	6	679	-460	65	-3	3	7	954	170	-61	-5	6	7	671	613	46	-4	9	7	789	-812	28
6	25	6	694	-726	82	1	31	6	630	-192	-134	-3	3	7	1484	1666	118	-7	6	7	584	530	37	-2	9	7	1058	1015	21
-6	26	6	155	-178	-155	2	31	6	517	-168	-97	-2	3	7	1393	1337	17	-3	6	7	2044	2131	21	-2	9	7	2104	2078	19
-5	26	6	361	-239	-145	3	31	6	151	-22	-151	-1	3	7	2196	-2317	16	-2	6	7	3157	-1178	20	-1	9	7	1129	1308	48
-4	26	6	1072	-985	46	-2	32	6	330	-112	-198	-1	3	7	879	-855	14	-1	6	7	1468	-1595	17	0	9	7	382	1880	48
-3	26	6	1086	1067	44	-1	32	6	166	-144	-86	-1	3	7	2551	-2555	18	0	6	7	225	34	-48	1	9	7	392	1880	20
-2	26	6	408	528	-121	0	32	6	354	-357	-100	-3	3	7	21	-389	-13	2	6	7	667	-705	26	2	9	7	227	-287	-112
-1	26	6	383	278	-103	1	32	6	401	471	-147	-3	3	7	1189	153	-22	2	6	7	2807	-2763	20	3	9	7	1303	-1277	24
0	26	6	1712	1689	23	2	32	6	541	-41	-95	-2	3	7	285	63	-88	3	6	7	941	-964	27	4	9	7	407	-389	-68
1	26	6	374	-286	-116	3	32	6	316	471	-316	-3	3	7	1432	1662	20	4	6	7	1011	-1040	31	5	9	7	1170	-1238	33
2	26	6	538	546	130	4	32	6	188	53	-122	-3	3	7	643	660	50	5	6	7	115	-236	-115	5	9	7	701	-770	54
3	26	6	138	244	-138	5	32	6	434	561	-332	-3	3	7	332	153	-66	6	6	7	1542	1579	29	7	9	7	308	-44	-145
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5	26	6	1290	-1240	44	-9	1	7	407	-350	-104	8	3	7	284	-498	-20	8	6	7	559	438	81	-9	10	7	443	-482	-126
6	26	6	408	-433	-131	-8	1	7	281	99	-151	-4	3	7	884	808	55	9	6	7	542	512	90	-8	10	7	583	-376	73
-3	27	6	701	695	69	-7	1	7	696	716	46	-4	3	7	444	399	-81	-8	7	7	511	67	84	-7	10	7	665	-698	62
-4	27	6	549	604	87	-6	1	7	1284	-1341	28	-9	4	7	947	1034	42	-9	7	7	141	265	-141	-6	10	7	317	-164	-112
-5	27	6	656	613	66	-5	1	7	215	342	-151	-5	3	7	947	1034	42	-9	7	7	141	265	-141	-6	10	7	317	-164	-112
-6	27	6	1324	1351	43	-4	1	7	353	391	53	-4	3	7	312	431	-78	-7	7	7	276	203	-152	-5	10	7	700	765	45
-7	27	6	897	-859	40	-3	1	7	1798	-1799	19	-5	4	7	1372	-1381	28	-6	7	7	1566	1042	34	-4	10	7	489	454	45
-8	27	6	897	-859	40	-3	1	7	1957	2000	17	-4	4	7	239	-11	-69	-5	7	7	1352	1393	27	-3	10	7	789	783	29

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

1	27	6	135	118-135	-1	1	105	1048	17	-2	4	7	656-656	28	-4	7	7	867	921	31	-2	10	7	703	711	28	
2	7	6	145	358-435	-1	1	150	1331	17	-2	4	7	2550-2551	18	-4	7	7	91	98	91	-1	10	7	92	73	92	
3	7	6	740	305-510	-1	1	53	386	16	-2	4	7	318	240	44	-2	7	7	262	271	18	0	10	7	105	-104	24
4	7	6	123	228-375	-1	1	73	591	16	-2	4	7	1241	1221	18	-2	7	7	673	684	17	2	10	7	1692	-1671	22
5	7	6	323	325-370	-1	1	783	491	16	-2	4	7	267	2451	19	-2	7	7	1576	1603	19	2	10	7	229	-158	126
6	7	6	363	171-231	-1	1	1234	1552	17	-2	4	7	802	764	29	-2	7	7	623	624	33	4	10	7	317	31	96
7	6	6	170	371-68	-1	1	419	128	-5	4	4	7	468	399	53	-2	7	7	505	397	41	5	10	7	123	210	123
8	6	6	139	713-95	-1	1	77	659	63	4	4	7	268	653	45	4	7	7	131	1165	29	6	10	7	377	649	51
9	6	6	316	613-95	-1	1	659	426	76	4	4	7	755	237	-41	4	7	7	1665	1330	28	7	10	7	470	487	93
10	6	6	305	613-95	-1	1	44	250	13	4	4	7	622	668	53	4	7	7	76	359	49	8	10	7	631	519	79
11	6	6	375	613-95	-1	1	42	20	15	4	4	7	737	672	66	4	7	7	133	115	23	9	10	7	635	520	79
12	6	6	370	613-95	-1	1	42	20	15	4	4	7	647	566	70	4	7	7	317	68	11	10	7	7	146	-20	144
13	6	6	370	613-95	-1	1	42	20	15	4	4	7	913	747	49	4	7	7	365	58	15	11	7	7	145	1094	43
14	6	6	370	613-95	-1	1	42	20	15	4	4	7	1380	1471	35	4	7	7	1356	126	40	12	7	7	521	-438	36
15	6	6	370	613-95	-1	1	42	20	15	4	4	7	169	1748	24	4	7	7	14	429	14	13	7	7	1302	3317	29
16	6	6	370	613-95	-1	1	42	20	15	4	4	7	196	1583	23	4	7	7	117	51	17	14	7	7	141	3319	27
17	6	6	370	613-95	-1	1	42	20	15	4	4	7	196	1583	23	4	7	7	777	828	36	15	7	7	135	-1338	24
18	6	6	370	613-95	-1	1	42	20	15	4	4	7	196	1583	23	4	7	7	220	2467	23	16	7	7	339	380	56
19	6	6	370	613-95	-1	1	42	20	15	4	4	7	196	1583	23	4	7	7	1776	1829	21	17	7	7	103	-1009	23
20	6	6	370	613-95	-1	1	42	20	15	4	4	7	196	1583	23	4	7	7	351	406	53	18	7	7	147	-1647	43
21	6	6	370	613-95	-1	1	42	20	15	4	4	7	196	1583	23	4	7	7	253	2594	18	19	7	7	124	1208	43
22	6	6	370	613-95	-1	1	42	20	15	4	4	7	196	1583	23	4	7	7	868	855	26	20	7	7	483	-464	44
23	6	6	370	613-95	-1	1	42	20	15	4	4	7	196	1583	23	4	7	7	1767	1796	20	21	7	7	736	-681	36
24	6	6	370	613-95	-1	1	42	20	15	4	4	7	196	1583	23	4	7	7	483	464	44	22	7	7	783	-681	36

	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S
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2	5	11	7	120	-63	-120	7	308	132	19			4	25	7	254	135	-254
3	5	11	7	374	-367	-120	7	308	132	19			4	25	7	137	-153	-137
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48	5	11	7	374	-367	-120	7	308	132	19			4	25	7	137	-153	-137
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5 12	7 652	735	56	8 15	7 416	539-144	-1 19	7 1055	1072	34	-4 23	7 284	-247-170	3 27	7 231	189-231
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7 12	7 417	-22	-98	7 16	7 581	-510-80	1 19	7 115	2037	80	-2 23	7 418	25-127	5 27	7 152	417-152
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-5 13	7 281	-14-119	-1 16	7 526	-476	46	7 19	7 150	180	-150	4 23	7 591	-150	11 27	7 583	393
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-2 13	7 1114	1142	25	2 16	7 1171	-1164	30	7 665	-446	64	-6 24	7 59	-152	14 27	7 150	166-150
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1 13	7 106	-18-104	5 16	7 128	-23	-128	4	7 966	978	41	-9 24	7 136	31	17 27	7 467	407
2 13	7 107	-49-107	6 16	7 859	768	53	-3 20	7 120	143	34	-4 24	7 39	-152	18 27	7 164	177
3 13	7 383	-218	-71	7 16	7 392	347-124	-2 20	7 1092	1145	35	-5 24	7 39	-152	19 27	7 443	380
4 13	7 280	164-130	-8 17	7 149	45-149	0 20	7 118	118	-118	118	-1 24	7 39	-152	20 27	7 151	115
5 13	7 213	-210-213	-6 17	7 144	109-144	1 20	7 824	-459	48	4	2 24	7 39	-152	21 27	7 951	-274
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7 13	7 142	116-142	-5 17	7 636	683	59	4 20	7 797	796	67	4 24	7 39	-152	23 27	7 376	330
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-6 14	7 1054	-973	34	0 17	7 2058	-1971	25	-7 21	7 139	91-139	8 24	7 39	-152	28 27	7 403	-219
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-4 14	7 1221	-1206	27	3 17	7 786	823	45	-4 21	7 1106	184	10 24	7 39	-152	30 27	7 972	-235
-3 14	7 1087	-1043	27	4 17	7 126	18-126	5	7 112	-112	135	11 24	7 39	-152	31 27	7 383	-370
-2 14	7 1087	-1043	27	5 17	7 929	941	49	-2 21	7 125	-212	12 24	7 39	-152	32 27	7 904	-219
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3 14	7 905	-896	33	7 17	7 340	47-144	2	7 135	-88	-135	17 24	7 39	-152	37 27	7 403	-219
4 14	7 576	491	56	-5 18	7 522	-314	83	3 21	7 195	-88	18 24	7 39	-152	38 27	7 519	-276
5 14	7 676	584	51	-6 18	7 296	328-155	4 21	7 1582	1488	34	-6 24	7 150	-150	39 27	7 335	173

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10PO	10PC	10S	H	K	L	10PO	10PC	10S	H	K	L	10PO	10PC	10S	
0 32	7 210	-10-120	-9 3	8 340	-291-139	-7 6	8 127	-41-127	-5 9	8 426	398	66	-3 12	8 1737	-1740	23	1 10PO 10PC 10S	
1 32	7 241	284-186	-8 3	8 1214	-1269	37	-6 6	8 567	41	52	-9 9	8 353	281	-63	-2 12	8 849	802	
-9 0	8 290	-990	46	-7 3	8 118	126-118	-5 6	8 1648	-1675	25	-3 9	8 1669	1683	21	-1 12	8 1454	1374	
-8 0	8 558	-52-154	-7 3	8 820	-848	37	-4 6	8 339	278	-68	-2 9	8 686	363	37	0 12	8 1025	937	
-7 0	8 573	554	61	-4 3	8 868	-910	32	-3 6	8 1112	1118	23	-1 9	8 1721	1166	22	1 12	8 2440	234
-6 0	8 489	-425	54	-5 3	8 1758	1707	21	-2 6	8 1004	-1014	22	0 9	8 1333	1142	20	2 12	8 155	21-105

8 2 8 479 -230 -85 -0 6 8 316 -334-153 -6 9 8 362 -304 -94 -4 12 8 729 -731 41 0 15 8 489 -472 64

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S	H	K	L	10FO 10FC 10S
1 15	8	413	550 -75	-7 19	8	315	-310-200	6 22	8	401	245-220	0 27	8	658	731 48
2 15	8	1543	1582 27	-6 19	8	343	230-149	-7 23	8	149	188-139	1 27	8	315	-163-177
3 15	8	671	679 44	-5 19	8	132	431-132	-6 23	8	390	-628-137	2 27	8	813	-824 66
4 15	8	800	767 46	-4 19	8	1082	-1134 40	-5 23	8	283	-346-232	3 27	8	305	-353-159
5 15	8	712	357 50	-3 19	8	301	-76-116	-4 23	8	993	937 60	4 27	8	777	-748 68
6 15	8	145	-320-145	-2 19	8	118	88-110	-3 23	8	126	112-126	5 27	8	461	570-144
7 15	8	517	-481-89	-1 19	8	640	-668 46	-2 23	8	153	415 38	6 27	8	331	379-188
8 15	8	150	-186-150	0 19	8	644	693 37	-1 23	8	1093	1116 38	7 27	8	556	470 81
-7 16	8	823	671 56	1 19	8	510	-508 67	0 23	8	171	-742 32	8 27	8	116	238-16
-6 16	8	663	539 63	2 19	8	194	-47-194	1 23	8	128	238-126	9 27	8	708	-626 61
-5 16	8	1149	-145 36	3 19	8	1082	1062 39	2 23	8	135	-731-126	0 28	8	576	-467 52
-4 16	8	1038	-1018 35	4 19	8	132	-181-132	3 23	8	187	-131 46	1 28	8	812	-898 61
-3 16	8	539	518 54	5 19	8	136	-124-136	4 23	8	142	78-143	2 28	8	153	-302-133
-2 16	8	1246	-1446 28	6 19	8	240	-286-240	5 23	8	143	78-143	3 28	8	356	144-114
-1 16	8	1419	1444 25	7 19	8	220	-383-228	6 23	8	151	-238-102	4 28	8	394	295-141
0 16	8	2344	2370 17	7 20	8	149	233-149	-6 24	8	508	712 71	5 28	8	950	-836 52
1 16	8	611	-947 44	-6 20	8	599	-674 76	-5 24	8	131	130-131	6 28	8	256	-144-256
2 16	8	559	321 60	-5 20	8	490	555 85	-4 24	8	102	580-331	7 28	8	219	-440-219
3 16	8	236	-110-112	-4 20	8	227	133-227	-3 24	8	325	-352-126	8 28	8	464	610-181
4 16	8	1165	-164 36	-3 20	8	887	-944 41	-2 24	8	327	372 74	9 28	8	149	314-149
5 16	8	132	-48-132	-2 20	8	1173	1260 34	-1 24	8	853	-822 70	0 29	8	152	4-152
6 16	8	94	-741 52	1 20	8	370	-310 79	0 24	8	1208	-181 38	1 29	8	931	929 56
7 16	8	786	-614 59	2 20	8	695	-732 38	1 24	8	138	330-138	2 29	8	646	-674 77
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-1 17	8	1068	-1010 48	4 20	8	1028	-1089 41	3 24	8	118	371-118	4 29	8	308	161-189
-2 17	8	327	-166-154	5 20	8	130	-215-130	4 24	8	605	697 72	5 29	8	188	262-122
-3 17	8	338	304-114	6 20	8	690	637 60	5 24	8	319	154-144	6 29	8	885	801 60
-4 17	8	814	-793 40	7 20	8	668	-494 59	-3 25	8	319	154-144	7 29	8	399	-358-152
-5 17	8	1162	1202 31	8 20	8	147	168-147	-4 25	8	111	-60-111	8 29	8	295	387-295
-6 17	8	1800	1837 26	9 20	8	296	358-296	-5 25	8	111	134-111	9 29	8	148	153-148
-7 17	8	430	-557 67	0 21	8	258	192-258	-6 25	8	778	-448 58	0 30	8	355	-164-102
-8 17	8	1170	1140 21	1 21	8	349	-128-111	-7 25	8	1030	100 48	1 30	8	440	-157-121
-9 17	8	628	-663 50	2 21	8	430	-629-80	-8 25	8	346	488 56	2 30	8	159	-241-159
0 17	8	1804	-1843 28	3 21	8	430	-629-80	0 26	8	29	588 53	3 30	8	150	-232-150
1 17	8	358	393 58	4 21	8	606	-330 56	1 26	8	49	588 53	4 30	8	150	-232-150
2 17	8	600	-534 59	5 21	8	428	430 71	2 26	8	91	885 52	5 30	8	250	-317-124
3 17	8	471	-604 89	6 21	8	466	-476 72	3 26	8	271	257-272	6 30	8	264	-271-264
4 17	8	882	849 56	7 21	8	466	-476 72	4 26	8	40	706 51	7 30	8	581	612 54
5 17	8	471	-604 89	8 21	8	466	-476 72	5 26	8	131	126-131	8 30	8	267	97-157
6 17	8	269	-103-269	9 21	8	492	515 83	6 26	8	38	120 51	9 30	8	643	-729 48
7 17	8	269	-103-269	0 22	8	269	103-192	-7 26	8	269	103-192	0 31	8	545	-621 39
8 17	8	269	-103-269	1 22	8	139	116-139	-8 26	8	269	103-192	1 31	8	545	-621 39
9 17	8	269	-103-269	2 22	8	140	191-140	-9 26	8	467	-556-191	2 31	8	545	-621 39
-0 18	8	274	233-266	3 22	8	140	191-140	-4 26	8	467	-556-191	3 31	8	545	-621 39

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 2

H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S	H	K	L	10FO	10FC	10S
-5	18	8	399	436	-96	6	21	8	520	-355	81	-3	26	8	138	189	-38	-3	14	9	335	351	59
-4	18	8	669	639	52	-7	22	8	116	5	-146	-2	26	8	645	-639	70	-2	1	9	863	856	71
-3	18	8	478	-379	66	-7	22	8	618	-631	78	-2	26	8	1011	995	46	-1	1	9	1780	-812	40
-2	18	8	511	-446	53	-5	22	8	288	-62	88	0	26	8	1119	1193	39	2	4	9	85	85	40
-1	18	8	212	-41	-212	-4	22	8	553	-398	68	1	26	8	140	-66	-140	4	4	9	311	-382	-83
0	18	8	753	-788	30	-3	22	8	248	-187	-248	2	26	8	1253	1287	46	4	4	9	2190	2201	35
1	18	8	403	-40	-80	-2	22	8	710	715	55	3	26	8	140	-13	-140	5	4	9	739	664	41
2	18	8	280	130	-118	-1	22	8	376	-399	-87	4	26	8	889	-828	58	7	4	9	132	-166	121
3	18	8	187	-25	-187	0	22	8	430	323	55	5	26	8	114	-168	-114	8	4	9	75	-774	59
4	18	8	502	424	77	1	22	8	1170	1336	39	-5	27	8	311	70	-218	9	4	9	998	1025	49
5	18	8	582	681	64	2	22	8	137	-385	-137	6	27	8	145	120	-145	-8	5	9	425	-268	-89
6	18	8	294	87	-222	3	22	8	127	239	-127	7	27	8	963	1111	52	-7	5	9	275	51	-142
7	18	8	495	214	-90	4	22	8	139	-73	-39	-2	27	8	886	496	82	-9	2	9	75	-48	136
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-5	5	9	2444	-2431	25	-3	8	9	1308	1307	23	-1	11	9	719	-736	32	3	14	9	303	-27	-102
-4	5	9	185	-363	-185	-2	8	9	3009	-3037	22	0	11	9	147	-219	-86	4	14	9	555	570	47
-3	5	9	928	-893	26	-1	8	9	2955	-3016	21	1	11	9	305	-12	-305	5	14	9	138	-26	-128
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6	5	9	1509	-1487	31	8	8	9	306	-183	-207	-8	12	9	113	102	0	5	15	9	351	350	52
7	5	9	730	-680	50	-9	8	9	236	763	59	-7	12	9	307	-320	-84	6	15	9	114	133	-114
8	5	9	321	705	-116	-10	8	9	765	767	59	-5	12	9	300	359	-120	7	15	9	1871	149	24
9	5	9	305	-61	-13	-11	8	9	352	-54	-17	-6	12	9	724	-797	31	8	15	9	236	-282	-196
0	6	9	266	-311	-237	-6	9	9	783	-742	46	-4	12	9	1745	-1697	21	9	15	9	489	-54	76
-1	6	9	1261	-1298	36	-6	9	9	561	525	48	-3	12	9	254	431	-107	4	15	9	408	37	-84
-2	6	9	791	-813	40	-4	9	9	264	-238	21	-2	12	9	180	-20	-180	5	15	9	709	-621	64
-3	6	9	380	-212	-73	-3	9	9	1738	-1696	22	0	12	9	224	-257	48	7	15	9	254	-42	-254
-4	6	9	303	-262	-81	-2	9	9	759	-766	30	1	12	9	1323	1251	24	8	15	9	411	-159	-114
-5	6	9	988	1015	29	0	9	9	1377	1407	15	2	12	9	791	881	36	-1	16	9	804	-676	55
-6	6	9	713	765	27	1	9	9	283	2415	22	3	12	9	653	-487	15	2	16	9	451	-483	97
-7	6	9	221	2248	57	2	9	9	907	-734	31	4	12	9	1333	1313	31	-3	16	9	370	-385	-238
-8	6	9	4564	-4531	21	3	9	9	935	911	33	5	12	9	526	-557	82	-4	16	9	123	-84	-129
-9	6	9	150	113	-150	4	9	9	570	472	49	6	12	9	525	559	87	-5	16	9	753	781	42
0	6	9	1363	-1365	26	5	9	9	1457	-1421	31	7	12	9	413	-309	-124	-6	16	9	436	744	50
1	6	9	1839	-1835	26	6	9	9	524	-399	70	8	12	9	413	-309	-124	-7	16	9	436	744	50
2	6	9	326	-239	-103	7	9	9	510	-557	-90	-9	13	9	134	-6	-134	-2	16	9	434	427	62

-1	23	9	502	34	62	1	21	9	682	53	53	52	-104	82	-1	5	10	292	209	180	9	10	13	-380	-82
0	23	9	646	65	55	2	28	9	133	52	-153	35	-174	44	-1	5	10	568	711	54	-5	10	387	-101	-12
1	23	9	500	64	70	3	28	9	121	93	63	35	-174	44	-1	5	10	233	132	67	-4	10	110	-35	-10
2	23	9	138	7	38	-4	28	9	614	525	83	35	114	65	-1	5	10	233	132	67	-3	10	470	-154	49
3	23	9	124	5	30	-3	28	9	397	205	-24	35	114	65	-1	5	10	450	417	59	-2	10	385	364	56
4	23	9	133	15	33	-2	28	9	315	208	-46	35	114	65	-1	5	10	415	359	50	-1	10	27	-367	73
5	23	9	334	-60	234	-1	28	9	148	-100	-46	35	114	65	-1	5	10	931	932	23	0	10	460	682	25
-6	24	9	430	-67	131	0	28	9	407	233	-53	35	114	65	-1	5	10	92	85	-62	1	10	89	884	30
-7	24	9	369	-73	135	1	28	9	780	719	-65	35	114	65	-1	5	10	155	1337	45	2	10	89	884	30

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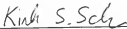
BIOGRAPHICAL SKETCH

I was born in 1968 in Williamsburg, Virginia, and my parents gave me the first name, Lucian, made famous by the Greek Satirist (see *Lucian: Satirical Sketches*; Paul Turner, Ed.), the middle name, Amerigo, after Amerigo Vespucci, the famous fifteenth century Italian explorer, and from my father I received the surname, Lucia (Latin: light). I attended schools in Bayonne, NJ until 1985 and transferred to Kissimmee, FL where I finished school in 1988. I attended the University of Florida at Gainesville, Florida for the last seven years, the latter five at the Department of Chemistry working toward my Ph.D in organic chemistry.

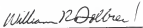
Some of the non-scientific books and pieces of literature which have influenced my personality and character include: *Murders in the Rue Morgue* by Edgar Allen Poe, *Morte d'Artur* by Thomas Mallory, Marvel Comics (1969-1979), *The Bear* by William Faulkner, and *Housetops* (published by *Slaves of the Immaculate Heart*). I also enjoy epistemology, medicine, electronics, athletics, and conundrums.

I will be at the University of Rochester in Rochester, NY as a postdoctoral fellow under Professor David G. Whitten and hope to someday teach, write, research, make a lot of money and have a big Italian family with all the trimmings.

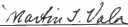
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Kirk S. Schanze, Chairman
Associate Professor of Chemistry

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William R. Dolbier
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Martin T. Vala
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


John R. Reynolds
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Stephen Schulman
Professor of Medicinal Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1996

Dean, Graduate School

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